Quality Assurance and Field Sampling Plan

CITY OF PORTSMOUTH, NEW HAMPSHIRE

FINAL DRAFT FOR APPROVAL

Background Water Quality Sampling in Support of the Future Pease NPDES Permit

June 1, 2018

Underwood Engineers, Inc.
Portsmouth, New Hampshire

Table of Contents

List of Figures

List of Tables

List of Appendices

Introduction

The City of Portsmouth requires water quality sampling in the Piscataqua River near the Pease and Newington Wastewater Treatment Facility (WWTF) combined discharge outfall. Results from this sampling effort will provide data to the City and New Hampshire Department of Environmental Services (NHDES) in support of making decisions on the future Pease National Pollutant Discharge Elimination System (NPDES) permit capacity and to support an Antidegradation Water Quality Study that will be performed by NHDES. This monitoring effort consists of sampling in the Piscataqua River upstream of the Pease and Newington Outfall. Concurrent effluent sampling will be performed at the Pease and Newington Wastewater Treatment Facilities. The WWTF effluent sampling includes 24-hour flow-weighted composite samples and effluent grab samples to fully characterize the water quality flows from the WWTFs to the Piscataqua River. The data will be summarized in a sampling report for submittal to the City, NHDES, and EPA.

This Quality Assurance and Field Sampling Plan (QAFSP) includes a discussion of the sampling plan rationale, sampling locations and figures, program management, a detailed list of analytical parameters, standard operating procedures, and the reporting framework. The QAFSP follows quality assurance (QA) and quality control (QC) measures detailed in this document.

1. Sampling Plan Rationale

This sampling program consists four (4) rounds of concurrent sampling at three (3) unique locations. Table 1 lists the sampling locations, the type of sampling that will be conducted, and category of analytical parameters. (The parameter categories are further explained in Section 3.1, Table 4.) The results of this study will provide data on the current water quality characteristics of the Piscataqua River during low flow conditions and the effluent water quality of both the Pease and Newington wastewater treatment facilities (WWTFs).

Table 1: Location and description of samples taken during this study.

Sampling Location	Sample Type	Parameters
Piscataqua River	Grab Sample	Laboratory
	In-Situ Measurements	Field
Pease WWTF Effluent	24-hour Flow-Weighted Composite	Laboratory
	Grab Sample	Field
Newington WWTF Effluent	24-hour Flow-Weighted Composite	Laboratory
	Grab Sample	Field

Piscataqua River Sampling

The Piscataqua River (River) sampling will be in the zone upstream of the Pease and Newington wastewater treatment facility combined outfall. Upstream in this situation is south of the outfall towards the ocean as the sampling will be conducted during the flood tide. The objective of the sampling is to measure background water quality during a tidal stage when the dilution of all sources of pollution, including contributions from the WWTFs, is at or near the lowest levels.

River sampling will be conducted during low flow conditions targeting the low to high tidal cycle during June and July of 2018. Based on NHDES guidance the difference between the low to high tide must be less than 6.5 feet and the grab samples must be taken 1 to 1.5 hours after local slack low tide. River samples will be taken from a boat approximately 200 to 300 feet upstream of the WWTF outfall (Figure 1) to minimize outfall and nearshore interferences. River samples will be collected from one location with approximate GPS coordinates N 43.102418, E -70.789591. GPS coordinates will be taken to ensure each sampling round is conducted in the same location. Samples will be taken 1-meter below the water surface to avoid possible floating material and boat interferences. Additional in-situ measurements using water quality meters will be conducted to record field parameters i.e. dissolved oxygen, temperature, pH, and conductivity (salinity) levels at the time of sampling. A total of four (4) sampling events have been identified that meet these criteria during June and July 2018 and are listed in Table 2. Backup dates (Appendix A) will be selected in the event that sampling efforts are unsuccessful due to rainfall occurrences, equipment failure, unsafe river conditions, WWTF issues, or other unforeseen circumstances.

Table 2: Details of sampling events in Piscataqua River

Date	Day	Time	Tide Height (ft)	Approximate River Sampling Time
6/6/2018	Wed	11:49	6.12	13:19
7/3/2018	Tue	21:56	6.27	23:26
7/8/2018	Sun	01:22	6.37	02:52
7/23/2018	Mon	03:12	6.49	04:42

Wastewater Treatment Facility Sampling

Sampling of the Pease and Newington WWTF's effluent will consist of 24-hour flow-weighted composite samples and grab samples. The flow-weighted composites will be generated over the 24-hour period ending on the day of the river sampling. Newington WWTF composite samples will be on a 7am to 7am schedule and Pease WWTF will be on an 8am to 8am schedule. The entire 24-hour composite sample period will take place prior to the River sampling. Therefore, if the River sampling is scheduled for anytime between 12am to 8am then the WWTF will shift one full day ahead of the River sampling. Table 3 lists the details of these sampling events. The flow-weighted composite samples will be generated using pre-programmed automated samplers that will take a predetermined sample aliquot after a specified volume of effluent water has passed the monitoring location. All aliquots are dispensed into a single 5.5-gallon container that is housed in a temperature-controlled compartment within the sampler. The purpose of a flow-weighted composite sample is to develop an aggregate concentration over the specified monitoring period that accounts for fluctuations in the effluent flow. At the end of the 24-hour period these samples are processed and shipped for laboratory analysis in accordance with sample processing protocols detailed in this QAFSP. The WWTF grab samples are taken at the end of each 24-hour composite sampling period and analyzed at the WWTF for field parameters, i.e. total residual chlorine, dissolved oxygen, temperature, pH, and conductivity (salinity).

Table 3: Details of concurrent sampling events at Newington (7am to 7am) and Pease (8am to 8am) wastewater treatment facilities.

COMPOSITE SAMPLES						GRAB SAMPLES		
Start			End					
Date	Day	Time	Date	Day	Time	Date	Day	Time
6/5/2018	Tues	7:00/8:00	6/6/2018	Wed	7:00/8:00	6/6/2018	Wed	7:00/8:00
7/2/2018	Mon	7:00/8:00	7/3/2018	Tue	7:00/8:00	7/3/2018	Tue	7:00/8:00
7/6/2018	Fri	7:00/8:00	7/7/2018	Sat	7:00/8:00	7/7/2018	Sat	7:00/8:00
7/21/2018	Sat	7:00/8:00	7/22/2018	Sun	7:00/8:00	7/22/2018	Sun	7:00/8:00

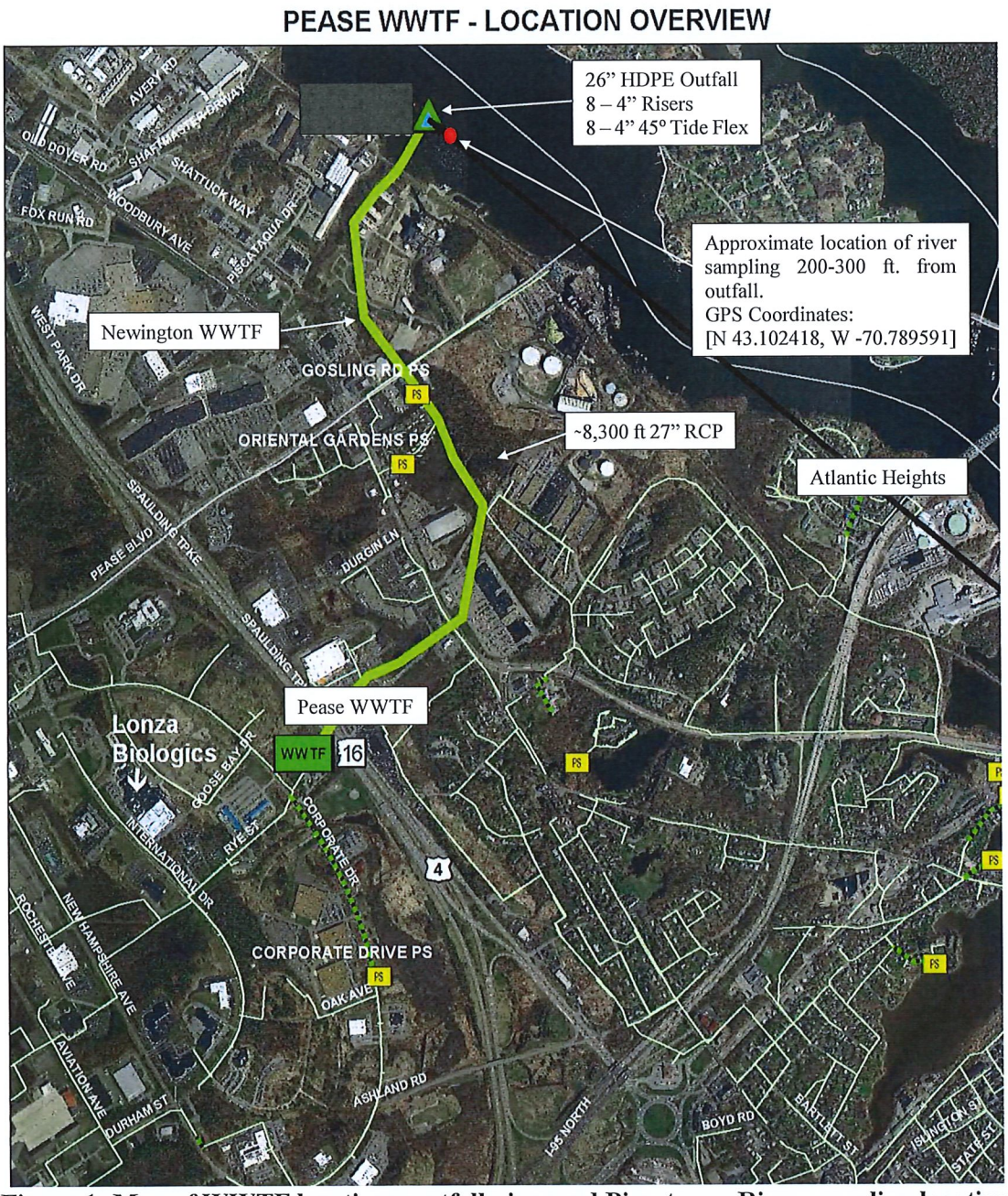


Figure 1: Map of WWTF locations, outfall pipe, and Piscataqua River sampling location.

1.1 Sampling Strategy

Sampling in the River and at both WWTFs will consist of the primary samples as well as quality control (QC) samples. The first round of sampling will include the full suite of QC samples for all locations consisting of field duplicates for laboratory parameters and field replicates for field parameters. In addition, trip blanks, equipment blanks, and matrix spike / matrix spike duplicates (MS/MSD) will be analyzed for metals, cyanide, total phenolic compounds, volatile organic compounds, acid extractable compounds, and base-neutral compounds. Sampling rounds 2 through 4 will have a reduced count of QC samples consisting of field duplicates at each location for ammonia as N, total Kjeldahl nitrogen, nitrate plus nitrite nitrogen, total phosphorus, and metals; field replicates at each location for field parameters; equipment blanks and MS/MSD analyzed for metals at each location. In addition, trip blanks of River samples will be analyzed for cyanide, total phenolic compounds, volatile organic compounds, acid extractable compounds, and base-neutral compounds. Tables of each round of sampling, QC samples, testing parameters, and the total project sample counts can be found in Appendix B of this QAFSP.

The River sampling will be conducted in accordance with the standard grab sampling protocol outlined in Appendix C. The in-situ measurements will adhere to the standard protocol for collection of water quality data with multi-parameter water quality meters outlined in Appendix D. Special attention will be given during field sampling activities to avoid obvious sources of metals contamination and to avoid protocols that could introduce metals contamination. Wherever possible, non-metal instruments and equipment will be used.

The River grab samples will be collected by boat (19' fiberglass, gas fueled) at 1-meter below the surface to avoid possible floating debris. The boat will be anchored and 3-5 min of water flow will be allowed prior to any sampling or measurements. Whenever possible, samples will be collected facing upstream and upwind to minimize introduction of contamination. The grab samples will be collected using a grab sampling technique. The principle of the grab technique is to fill a sample bottle by rapid immersion in water and capping to minimize exposure to airborne particulate matter. The grab samples will be collected using the "Clean Hands" technique (EPA Method 1669 - Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels) as outlined in Appendix E. QC sample requirements are summarized in Appendix B and discussed in Section 4.2.

The samples will be picked up by EnviroSystems laboratory personnel and delivered to Hampton, New Hampshire for the required analyses. Sampling details including sample date, sample time, analytical parameters, and preservation type will be recorded on the chain-of-custody (COC) form (Appendix F). Chain-of-custody protocol will be followed during any transfer of the samples (i.e., from City personnel to Underwood Engineers staff and from Underwood Engineers staff to EnviroSystems staff). River samples that will be analyzed for trace metals will be filtered in the field following trace metals sample handling protocols outlined in Appendix E. Samples prepared for trace metals analysis will be packaged and shipped to Eurofins Frontier Global Sciences in Bothell, Washington.

The in-situ field measurements will be conducted using a multi-parameter water quality meter (i.e., YSI 6600 or equivalent) to record measurements of dissolved oxygen, temperature, pH, and conductivity (salinity). Field data will be recorded using the field meter as well as recorded in a field notebook. Details of the YSI 6600 are included in Appendix D. The water quality meter

will be calibrated by field personnel prior to and following each sampling round following the manufacturer's standard protocols. Field replicates consisting of two or more field measurements collected sequentially while in the field will be conducted to assess the precision of the measurements in relation to the instrument variability and sampler error, as well as changing water conditions with flowing tidal water. Replicate values will be recorded in the field notebook.

The WWTF effluent sampling by the City personnel will be conducted in accordance with their own standard sampling protocols and adhere to the standard level of quality assurance and quality control measures. The WWTF effluent sample will consist of a 24-hour composite sample collected during the 24-hour period prior to the planned River sampling time as detailed in Table 3. WWTF grab samples will be collected at the completion of the 24-hour composite sample timeframe, delivered to EnviroSystems, and analyzed for the following laboratory parameters: fecal coliform, enterococci, oil and grease, turbidity, and VOC. Additional grab samples will be collected and analyzed at the WWTF for the following field parameters: total residual chlorine, dissolved oxygen, temperature, pH, and conductivity (salinity). Replicate field measurements will be recorded for verification of results.

WWTF composite and grab samples will be picked up by Underwood Engineers personnel at the WWTF, packaged with the River samples, and delivered to either EnviroSystems or Eurofins Frontier Global Sciences for analyses. See Table 4 for the project sample matrix detailing sampling location, analytical parameters, and analytical laboratory.

2. Sampling Locations

Figure 1 above depicts the locations of the Newington and Pease WWTFs, the combined WWTF outfall, and the Piscataqua River sampling location. The sampling locations are listed as follows:

1. Pease WWTF Effluent 24-hour composite sample referred to as PEASE_001C
2. Pease WWTF Effluent grab sample referred to as PEASE_001G
3. Newington WWTF Effluent 24-hour composite sample referred to as NEW_001C
4. Newington WWTF Effluent grab sample referred to as NEW_001G
5. Piscataqua River grab sample referred to as RIVER_001G

Sample naming format is LOCATION_SAMPLE ROUND C or G. The first sample round as written above is 001, second sample round is 002, and so forth. The C is for flow-weighted composite sample and the G is for grab sample.

3. Program Management and Organization

Project team members include staff from the City of Portsmouth Department of Public Works, OspreyOwl Environmental, Underwood Engineers, Eurofins Frontier Global Sciences, and EnviroSystems. A summary of the key personnel along with their primary responsibilities is presented below:

- **Mr. Terry Desmarais (P.E.)** is the lead contact for the project for the City of Portsmouth Department of Public Works. Mr. Desmarais will be responsible for approving this QAFSP and coordinating all project efforts.

- **Mr. Patrick Wiley (Ph.D.)** is the wastewater operations manager for the City of Portsmouth Department of Public Works. Mr. Wiley will be responsible coordinating WWTF sample collection and providing WWTF access for the sampling team.
- **Ms. Paula Anania** is the chief plant operator for the City of Portsmouth Wastewater division. Ms. Anania will be responsible for assisting WWTF sampling team on sample collection, in-house grab sample analyses, and preparation of samples for delivery to analytical laboratories.
- **Mr. Ricardo Cantu** of OspreyOwl Environmental, LLC is a subconsultant responsible for ensuring "clean sampling" collection and analysis techniques for the WWTF effluent monitoring. Mr. Cantu will work with plant operators, City personnel, and Underwood Engineers staff on the collection, in-house analyses, and sample preparation for delivery to analytical laboratories.
- **Mr. Steve Clifton (P.E.)** of Underwood Engineers will be the project manager and will be responsible for ensuring that all field data and samples are collected in accordance with this QAFSP. Mr. Clifton will be responsible for review and submittal of all deliverables required under this project.
- **Mr. Tim Puls (P.E.)** of Underwood Engineers will be the field project manager. Mr. Puls will be responsible for preparation of the QAFSP and for coordinating the field schedule during the sampling program.
- **Mr. Steve Jones (Ph.D.)** of University of New Hampshire is the lead person for the Piscataqua River sampling efforts. Mr. Jones will coordinate with Underwood Engineers on sampling schedule as well as river sample collection, preparation, and delivery to the analytical laboratories.
- **Ms. Amanda Komarek** will be the primary laboratory contact at EnviroSystems. Ms. Komarek will be responsible for preparation and delivery of sampling kits to Underwood Engineers prior to each sampling round as well as ensuring samples are analyzed at EnviroSystems in accordance with this QAFSP. Ms. Komarek will also provide the laboratory reports to Underwood Engineers following each sampling round.
- **Mr. Robert Brunette** will be the primary laboratory contact at Eurofins Frontier Global Systems. Eurofins was selected for their capacity to conduct trace clean metals techniques in accordance with EPA Method 1669 (Appendix E). Mr. Brunette will be responsible for preparation and delivery of sampling kits to Underwood Engineers prior to each sampling round as well as ensuring samples are analyzed at Eurofins in accordance with this QAFSP. Mr. Brunette will also provide the laboratory reports to Underwood Engineers following each sampling round.

4. Sampling Parameters and Sampling SOPs

Sampling of Piscataqua River and the Pease and Newington WWTFs effluent will involve collection of grab samples, generation of 24-hour composite samples, and in-situ measurements. Samples will be analyzed for either laboratory or field parameters by one of two analytical laboratories, field sampling personnel, or WWTF personnel. Coordination of sample collection, field processing, packaging, and delivery to the respective labs will be conducted by Underwood Engineers. The project sample matrix including analytical methods is listed in Table 4.

Table 4: Project sample matrix including analytical parameters, sample source, analytical method, and entity responsible for testing.

SAMPLE MATRIX				
Laboratory Parameter	**River**	**WWTF**	**Analytical Method**	**Laboratory**
Biochemical Oxygen Demand (BOD_5)	Grab	24-hour Comp	SM 5210 B	EnviroSystems
Enterococci & Fecal Coliform	Grab	Grab	SM 92222 D	EnviroSystems
Total Suspended Solids (TSS)	Grab	24-hour Comp	SM 2540 D	EnviroSystems
Total Dissolved Solids (TDS)	Grab	24-hour Comp	SM 2540 C	EnviroSystems
Ammonia as N (NH3-N)	Grab	24-hour Comp	SM 4500-NH3 G	EnviroSystems
Chlorine (Total Residual)	NA	Grab	SM 4500-Cl D	WWTF
Total Kjeldahl Nitrogen (TKN)	Grab	24-hour Comp	SM 4500-NH3 G	EnviroSystems
Nitrate + Nitrite as Nitrogen	Grab	24-hour Comp	SM 4500-NO3 F	EnviroSystems
Oil and Grease	Grab	Grab	EPA 1664 A	EnviroSystems
Total Phosphorus	Grab	24-hour Comp	SM 4500-P E	EnviroSystems
Turbidity (NTU)	Grab	Grab	SM 2130 B	EnviroSystems
Total Phenols	Grab	24-hour Comp	EPA 420.1	EnviroSystems
Volatile Organic Compounds	Grab	Grab	EPA 624	EnviroSystems
Acid-Base-Neutral Extractable Compounds (ABNs)	Grab	24-hour Comp	EPA 625 / 8270	EnviroSystems
Total Recoverable Metals (Sb, As, Be, Cd, Cr, Cu, Fe, Pb, Ni, Se, Ag, Tl, Zn)	NA	24-hour Comp	EPA 200.8 CWA Trace Metals	Eurofins FGS
Total Hg	NA	24-hour Comp	EPA 1631 E	Eurofins FGS
Total Cyanide (CN)	NA	24-hour Comp	SM 4500-Cn E	Eurofins FGS
Total Recoverable Metals (Sb, Be, Cr, Fe, Tl)	Grab (unfiltered)	NA	EPA 200.8 CWA Trace Metals	Eurofins FGS
Dissolved Metals (As, Cd, Cu, Pb, Ni, Se, Ag, Zn)	Grab (filtered)	NA	EPA 1640 RP	Eurofins FGS
Total Cyanide (CN)	Grab (unfiltered)	NA	SM 4500-Cn E	Eurofins FGS
Dissolved Hg	Grab (filtered)	NA	EPA 1631 E	Eurofins FGS
Field Parameter				
Dissolved Oxygen	In-Situ	Grab	Field Meter	Field Team / WWTF
Temperature	In-Situ	Grab	Field Meter	Field Team / WWTF
pH	In-Situ	Grab	Field Meter	Field Team / WWTF
Conductivity	In-Situ	Grab	Field Meter	Field Team / WWTF

4.1. Metals Sampling and Analysis

Special attention is given to sample collection and analysis of total recoverable and dissolved metals. Selection of Eurofins Frontier Global Sciences (Eurofins) for all metals testing is based on their capacity to conduct trace metals techniques for seawater sampling. Eurofins will conduct metals testing in accordance with EPA Method 1669 *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*, Appendix E. Field sampling will also adhere to Method 1669 criteria which requires all sampling equipment and sample containers are cleaned in a laboratory or cleaning facility using detergent, mineral acids, and reagent water. These techniques are required to obtain the minimum reporting limit and minimum detection limits achievable. Most of the metals listed have minimum marine acute and chronic criteria levels based on NHDES Env-Wq rule 1703.21 Water Quality Criteria for Toxic Substances, effective December 1, 2016. An excerpt from Table 1703-1 is included as Table 5, which lists the acute and chronic criteria levels for both fresh and marine waters and the human health criteria for water and fish consumption for the list of target parameters.

Table 5: Excerpt from Table 1703-1 in NHDES Env-Wq rule 1700 Surface Water Quality Standards

Table 1703-1: Water Quality Criteria For Toxic Substances

CAS Number	Chemical Name	Protection of Aquatic Life Concentration in micrograms per liter (µg/l)				Protection of Human Health Units per Liter	
		Fresh Acute Criteria	Fresh Chronic Criteria	Marine Acute Criteria	Marine Chronic Criteria	Water & Fish Ingestion	Fish Consumption Only
7440360	Antimony	9,000	1,600	--	--	5.6 µg	640 µg
7440382	Arsenic	340	150	69	36	18 ng	140 ng
7440417	Beryllium	130	5.3	--	--	Note 1	--
7440439	Cadmium	0.39	0.21	33	7.9	Note 1	--
16065831	Chromium +3	152	19.8	10,3000	--	Note 1	--
7440508	Copper	2.9	2.3	4.8	3.1	1,000 µg	1,000 µg
57125	Cyanide	22	5.2	1.0	1.0	140 µg	140 µg
7439896	Iron	--	1,000	--	--	0.3 mg	--
7439921	Lead	10.5	0.41	210	8.1	--	--
7439976	Mercury	1.4	0.77	1.8	0.94	0.05 µg	0.051 µg
7440020	Nickel	120	13.3	74	8.2	610 µg	4,600 µg
7782492	Selenium	--	5	290	71	170 µg	4,200 µg
7440224	Silver	0.20	--	1.9	--	105 µg	65 mg
7440280	Thallium	1,400	40	2,130	--	0.24 µg	0.47 µg
744066	Zinc	30.0	30.0	90	81	5,000 µg	5,000 µg

4.2. Quality Assurance for Data Collection and Analyses

Quality control tasks involve planning for the type and number of quality control samples to be collected as well as several routine technical activities. The technical activities include but are not limited to:

- Calibration of field instruments according to manufacturer's specifications and record of calibrations results in field notebooks
- Preparation of field sample bottles (e.g., rinsed, sterilized, preservative added, cleaned in accordance with EPA Method 1669 for metals, etc.) prior to sample collection
- Preparation of field data sheets and log books
- Preparation of sample labels

A general overview of water quality monitoring sampling protocols can be found in Appendix G by the NH Volunteer River Assessment Program, which provides information on proper preparation of sample containers and the preservation of samples.

4.2.1. Quality Control Samples

The type and number of QC samples has been established based on a total of four rounds of sampling at three monitoring locations, i.e. Piscataqua River, Pease WWTF, and Newington WWTF. See Appendix B for a detailed table of the sample types and counts that will be collected for this project. The type of QC samples includes field duplicates for laboratory parameters, field replicates for field parameters, trip blanks, equipment blanks, matrix spike and matrix spike duplicates. For a detailed description and rationale of each QC sample type see Table 6. The

number of quality control samples is consistent with EPA quality control guidance (The Volunteer Monitor's Guide to Quality Assurance Project Plans, September 1996, EPA 841-B-96-003) and the NHDES Ambient River Monitoring Program. See Section 1.1 of this QAFSP and Appendix B for additional detail on each sampling round.

Table 6: Description and rationale of quality control samples.

Quality Control Sample Type	Sample Description	Rationale
Equipment Blank	Blank (deionized) water passed through equipment in the field and collected in the same manner used to collect water quality samples.	To verify that decontamination procedures are adequate and that field and laboratory protocols and procedures do not contaminate samples.
Trip Blank	Blank (deionized) water placed in sample container by the laboratory, carried to the study site with other bottles and equipment, and returned to the laboratory unopened for analysis.	To verify that the shipping, handling, and intermittent storage of containers does not result in contamination or cross-contamination of samples
Duplicate Sample	Two water quality samples collected sequentially for the same analytes.	To assess the combined effects of field and laboratory procedures on the measurement variability.
Replicate Sample	Two or more field sample measurements (dissolved oxygen, temperature, pH, conductivity) collected sequentially while in the field.	To assess the precision of measurement in relation to instrument variability and sampler error
Spike Matrix	A sample of either river or WWTF effluent water to which a spike solution is added (spikes will be for metals).	To assess the recovery bias and variability in relation to different water matrices.

4.2.2. Data Management Tasks

All relevant field and laboratory data will be provided in a hard copy report and electronic form. The field data documentation will be recorded in field notebooks appropriate for the sampling location and will include the following:

- Date, time, and name of technician(s) present while conducting sampling
- Field equipment checklist to ensure all necessary equipment is present when initiating field sampling trips
- Site conditions i.e. weather, river condition, presence of excessive debris or unknown substances in water that may contaminate sample
- Record of recent rain events or antecedent dry period
- Disturbance in normal operations at WWTF that may influence sample

For preservation, scanned copies of all handwritten field notes shall be made as soon as possible after each sampling event and saved on a database that can be accessed by the project manager.

4.2.3. Data Verification and Validation Tasks

Water quality data are verified by referencing replicate samples, reviewing critical ranges, reviewing consistency of spiked samples, and reviewing duplicate samples. The data are screened for outliers, with outliers being highlighted and examined to determine the cause of the deviation.

4.2.4. Measurement Performance Criteria for Water Quality Measurements

The measurement performance criteria for data associated with all matrices include considerations for precision, accuracy, representativeness, completeness, and comparability (PARCC). To meet PARCC requirements, quality control criteria are provided in the standard laboratory methodologies. These criteria include the use of field duplicates, field replicates, matrix spike samples, and calibration results to assess precision; calibration results, trip blanks, equipment blanks, and matrix spikes to assess accuracy and bias; blank samples to determine representativeness. The amount (percentage) of valid data obtained will be used to determine completeness.

An overview of the measurement performance criteria to be used in this study for water samples is listed in Table 7 and explained in more detail below it. The specific performance criteria goals and related information for each analyte/measurement are listed in Table 8.

Table 7: Data quality indicators (PARCC) requirements and measurement performance criteria.

Data Quality Indicators	Measurement Performance Criteria	RPD Value	QC Sample and/or Activity Used to Assess Measurement Performance
Precision-Overall	RPD	RPD $\leq$ 10%	Field Duplicates Field Replicates
Precision-Lab	RPD	RPD $\leq$ 10%	Matrix Spike Samples Sensor Calibration results
Accuracy / Bias	RPD	RPD $\leq$ 10%	Sensor Calibration Results Trip Blanks Field Blanks Laboratory Fortified Matrix Spikes
Representativeness	Adherence to field and lab protocols	RPD $\leq$ 10%	Field Duplicates Field Replicates
Comparability	Measurements should follow standard methods that are repeatable		All project personnel will review QAFSP and previous City of Portsmouth Water Quality Study, 2014
Completeness	Number of samples meeting data quality objectives		Data Completeness Check > 90% valid water quality results

Precision

Field duplicates or field replicates are collected for all parameters for the first sampling round and for select parameters for each successive sampling round (Appendix B). Field duplicates are physical water quality duplicate samples to assess environmental variability as well as strict

adherence to field sampling and laboratory techniques. Field replicates are repeated measurements to assess instrument variability using water quality sensors.

Precision goals vary according to specific pollutant but should remain within a threshold of 10% relative percent difference. The relative percent difference (RPD) will be calculated as follows:

$$RPD = \left(\frac{|x_1 - x_2|}{\frac{x_1 + x_2}{2}} \right) \times 100$$

where the equation numerator is the absolute value of the difference between duplicates and denominator is the average of the duplicates. RPD will be calculated for each set of duplicates and replicates for each round of sampling and reported to the City.

Accuracy

The water quality sensors calibration accuracy will be checked against standard solutions prior to each usage. If the standard solution is not measured within ±10% RPD of the known value the instrument will be recalibrated prior to field use. A two-point calibration procedure will be used, as specified by the manufacturer of the instrument to encompass the range of values typically encountered in similar systems. All calibration data will be documented in the field log books.

Trip blanks are deionized water aliquots that are bagged and sealed according to standard sampling protocols (Table 6) and brought into the field to assess contamination from typical field sampling procedures. For data to be precise and credible trip blanks should return below or at analytical detection limits 100% of the time.

Equipment blanks are collected at least one sampling event and consist of distilled water aliquots that are conveyed through existing sampling equipment under field conditions and are analyzed to detect any contamination from sampling methodology, and cross-contamination from previously collected samples. For data to be precise and credible, equipment blanks should return below or at analytical detection limits 100% of the time.

Representativeness

Representativeness is a measure of the degree to which data accurately and precisely represent a characteristic of a population at a sampling point or for a process condition or environmental condition. Representativeness is achieved through the consistent use of documented procedures for field sampling and handling process and through consistent adherence to laboratory methods.

Many water quality parameters are spatially and temporally dynamic, and experience near-limiting ambient conditions (e.g., low stream flow, warm water temperature) typically during the summer. For example, dissolved oxygen concentrations are typically least during the early morning hours in response to photosynthetic/respiration cycles. Decisions as to sampling location and time will represent the water quality parameters of interest in their expected abundance in the sample.

Comparability
Consistent data collection techniques and analytical parameters will support meaningful comparisons of gathered data. Water quality data will be compared to results in a previous related study, *City of Portsmouth Peirce Island Wastewater Treatment Facility and Piscataqua River Water Quality FINAL Report, September 2014.* A comparison of the water quality results and the laboratory and field sampling protocols followed for each monitoring effort will help to inform the repeatability of the study. For this project, comparability is attempted through the use of similar field sampling procedures, analytical methods, certified calibration standards, and representative sampling locations.

Completeness
Completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements expected to be obtained under normal conditions. For analytical methods, completeness is based on the number of valid results generated over a specific period compared to the number of results expected.

The quality objective for completeness for analyses performed by the analytical laboratory is 90-95 percent valid data for water quality results, collected during four (4) sampling rounds at each location for each sample type, for the analytes listed in Table 4. The ability to meet or exceed the completeness objective is dependent on the nature of samples submitted for analysis.

4.2.5. Quantification Limits

Each analytical method has a method detection limit (MDL) and method reporting limit (MRL), which are defined as follows and listed in Table 8.

Method Detection Limit (MDL)
The smallest concentration of analyte which may be detected by the entire analytical method including any sample preparation steps. It may be determined using replicate spike samples or calibration standards. The detection limit is calculated using the appropriate student's t parameter times the standard deviation of a series of spiked samples or standards. The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. (Absolute Resource Associates, Lab QA Manual, 2004)

Method Reporting Limit (MRL)
The lowest amount of an analyte in a sample that can be quantitatively determined with stated, acceptable precision and accuracy under stated analytical conditions (i.e. the lower limit of quantitation). Therefore, analyses are calibrated to the MRL, or lower. To take into account day-to-day fluctuations in instrument sensitivity, analyst performance, and other factors, the MRL is established at three times the MDL (or greater). (www.caslab.com)

Table 8: Method detection limit (MDL) and method reporting limit (MRL) for all target parameters in this project.

Laboratory Parameter	Analytical Method	MDL	MRL	Units
Biochemical Oxygen Demand (BOD_5)	SM 5210 B		5	mg/L
Enterococci & Fecal Coliform	SM 92222 D		1	CFU/100mL
Total Suspended Solids (TSS)	SM 2540 D	0.4	10	mg/L
Total Dissolved Solids (TDS)	SM 2540 C	0.4	10	mg/L
Ammonia as N (NH_3-N)	SM 4500-NH3 G	0.1	0.1	mg/L
Chlorine (Total Residual)	SM 4500-Cl D		0.02	mg/L
Total Kjeldahl Nitrogen (TKN)	SM 4500-NH3 G	0.1	0.1	mg/L
Nitrate + Nitrite as Nitrogen (NO_3 + NO_2 as N)	SM 4500-NO3 F	0.008	0.05	mg/L
Oil and Grease	EPA 1664 A		10	mg/L
Total Phosphorus (TP)	SM 4500-P E	0.008	0.02	mg/L
Turbidity	SM 2130 B			NTU
Total Phenols	EPA 420.1		0.05	mg/L
Volatile Organic Compounds (VOC)	EPA 624		5	µg/L
Acid-Base-Neutral Extractable Compounds (ABNs)	EPA 625 / 8270		5	µg/L
Total Recoverable Metals - Fresh Water (CWA Trace Metals)				
Antimony (Sb)	EPA 200.8	0.009	0.02	µg/L
Arsenic (As)	EPA 200.8	0.1	0.3	µg/L
Beryllium (Be)	EPA 200.8	0.004	0.06	µg/L
Cadmium (Cd)	EPA 200.8	0.008	0.02	µg/L
Total Chromium	EPA 200.8	0.02	0.1	µg/L
Copper (Cu)	EPA 200.8	0.02	0.1	µg/L
Iron (Fe)	EPA 200.8	1.1	10	µg/L
Lead (Pb)	EPA 200.8	0.005	0.04	µg/L
Nickel (Ni)	EPA 200.8	0.04	0.1	µg/L
Selenium (Se)	EPA 200.8	0.44	0.6	µg/L
Silver (Ag)	EPA 200.8	0.002	0.02	µg/L
Thallium (Tl)	EPA 200.8	0.006	0.02	µg/L
Zinc (Zn)	EPA 200.8	0.16	0.5	µg/L
Total Mercury (Hg)	EPA 1631 E	0.0834	0.5	ng/L
Total Cyanide (CN)	SM 4500-CN E	0.007	0.02	mg/L
Total Recoverable Metals - Seawater (CWA Trace Metals)				
Antimony (Sb)	EPA 200.8	0.09	0.2	µg/L
Beryllium (Be)	EPA 200.8	0.04	0.6	µg/L
Total Chromium	EPA 200.8	0.2	1.0	µg/L
Iron (Fe)	EPA 200.8	11	100	µg/L
Thallium (Tl)	EPA 200.8	0.06	0.2	µg/L
Total Cyanide (CN)	SM 4500-CN E	0.007	0.02	mg/L

Dissolved Metals in Seawater				
Arsenic (As)	EPA 1640 RP	0.0395	0.375	µg/L
Cadmium (Cd)	EPA 1640 RP	0.0203	0.1	µg/L
Copper (Cu)	EPA 1640 RP	0.078	0.25	µg/L
Lead (Pb)	EPA 1640 RP	0.02	0.1	µg/L
Nickel (Ni)	EPA 1640 RP	0.0751	0.25	µg/L
Selenium (Se)	EPA 1640 RP	0.156	1.5	µg/L
Silver (Ag)	EPA 1640 RP	0.01	0.1	µg/L
Zinc (Zn)	EPA 1640 RP	0.139	0.5	µg/L
Dissolved Hg	EPA 1631 E	0.0834	0.5	ng/L

5. Reporting

Reporting for this project will include water quality results delivered to the City after each round of sampling and a final report summarizing the monitoring effort and the water quality results from the project. The individual sampling round results will be delivered to the City as soon as made available from the laboratories and WWTF personnel. The final report will first be made available to the City in draft form for their input. A final version will then be produced by Underwood Engineers and delivered to the City for project close out.

APPENDIX A - SAMPLING BACKUP DATES

Date	Day	Time	Pred	High/Low	Approx. River Sample Time	WWTF Sample Start Date at 07:00 hrs Newington and 08:00 hrs Pease
6/2/2018	Sat	21:01	1.3	L		
6/3/2018	Sun	09:37	0.47	L		
6/3/2018	Sun	21:44	1.43	L		
6/4/2018	Mon	10:19	0.64	L		
6/4/2018	Mon	22:30	1.53	L		
6/5/2018	Tue	11:03	0.77	L		
6/5/2018	Tue	23:19	1.57	L		
6/6/2018	Wed	11:49	0.86	L	13:19	6/5/2018 Tues
6/7/2018	Thu	00:12	1.52	L		
6/7/2018	Thu	12:38	0.89	L		
6/8/2018	Fri	01:07	1.35	L		
6/9/2018	Sat	02:02	1.05	L		
7/2/2018	Mon	21:14	1.22	L		
7/3/2018	Tue	21:56	1.25	L	23:26	7/2/2018 Mon
7/4/2018	Wed	22:42	1.24	L		
7/5/2018	Thu	23:32	1.17	L		
7/7/2018	Sat	00:25	1.03	L		
7/8/2018	Sun	01:22	0.78	L	02:52	7/6/2018 Fri
7/23/2018	Mon	03:12	0.48	L	04:42	7/21/2018 Sat
8/20/2018	Mon	01:42	0.69	L		
8/20/2018	Mon	13:54	1.18	L		
8/21/2018	Tue	02:42	0.73	L		
8/21/2018	Tue	14:51	1.27	L		
8/22/2018	Wed	03:37	0.67	L		
8/22/2018	Wed	15:43	1.22	L		
8/23/2018	Thu	04:25	0.56	L		
9/17/2018	Mon	00:04	0.68	L		
9/17/2018	Mon	12:18	1.31	L		
9/18/2018	Tue	01:05	0.89	L		
9/18/2018	Tue	13:18	1.49	L		
9/19/2018	Wed	02:05	0.97	L		
9/19/2018	Wed	14:17	1.5	L		
9/20/2018	Thu	03:00	0.91	L		
9/20/2018	Thu	15:11	1.36	L		
9/21/2018	Fri	03:50	0.78	L		
9/21/2018	Fri	16:00	1.14	L		

Selected Dates

APPENDIX B - SAMPLE COUNT TABLES

Laboratory Parameters	First Sample Round											
	Total Sampling Frequency			No. of Field Duplicates[1]			No of Other QC Samples [2]			Total No. of Samples to Laboratory		
	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington
Biochemical Oxygen Demand	1	1	1	1	1	1	0	0	0	2	2	2
Enterococci	1	1	1	1	1	1	0	0	0	2	2	2
Fecal Coliform	1	1	1	1	1	1	0	0	0	2	2	2
Total Suspended Solids	1	1	1	1	1	1	0	0	0	2	2	2
Ammonia as N	1	1	1	1	1	1	0	0	0	2	2	2
Total Residual Chlorine	0	1	1	0	1	1	0	0	0	0	2	2
Total Kjeldhal Nitrogen	1	1	1	1	1	1	0	0	0	2	2	2
Nitrate plus Nitrite Nitrogen	1	1	1	1	1	1	0	0	0	2	2	2
Oil and Grease	1	1	1	1	1	1	0	0	0	2	2	2
Total Phosphorus	1	1	1	1	1	1	0	0	0	2	2	2
Total Dissolved Solids	1	1	1	1	1	1	0	0	0	2	2	2
Turbidity (NTU)	1	1	1	1	1	1	0	0	0	2	2	2
Metals	1	1	1	1	1	1	2 [3]	2 [3]	2 [3]	4	4	4
Cyanide	1	1	1	1	1	1	2 [4]	1 [5]	1 [5]	4	3	3
Total Phenolic Compounds	1	1	1	1	1	1	2 [4]	1 [5]	1 [5]	4	3	3
Volatile Organic Compounds	1	1	1	1	1	1	2 [4]	1 [5]	1 [5]	4	3	3
Acid Extactable Compounds	1	1	1	1	1	1	2 [4]	1 [5]	1 [5]	4	3	3
Base-Neutral Compounds	1	1	1	1	1	1	2 [4]	1 [5]	1 [5]	4	3	3
Field Parameters	First Sample Round											
	Total Sampling Frequency			No. Field Replicates [1]			No of Other QC Samples [2]			Total No. of Samples in Field		
	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington
Dissolved Oxygen	1	1	1	1	1	1	0	0	0	2	2	2
pH	1	1	1	1	1	1	0	0	0	2	2	2
Conductivity	1	1	1	1	1	1	0	0	0	2	2	2
Temperature	1	1	1	1	1	1	0	0	0	2	2	2

[1] - Includes Field Duplicates for Laboratory Samples and Field Replicates for Field Samples (In-situ)

[2] - Includes Trip Blanks (T), Equipment blanks (E), and Matrix Spike/Matrix Spike Duplicates(S)

[3] - Includes Equipment blank (E), and Matrix Spike/Matrix Spike Duplicates(S)

[4] - Includes Trip Blank (T) and Equipment blank (E)

[5] - Includes Equipment blank (E)

Laboratory Parameters	Second Sample Round											
	Total Sampling Frequency			No. of Field Duplicates[1]			No of Other QC Samples[2]			Total No. of Samples to Laboratory		
	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington
Biochemical Oxygen Demand	1	1	1	0	0	0	0	0	0	1	1	1
Enterococci	1	1	1	0	0	0	0	0	0	1	1	1
Fecal Coliform	1	1	1	0	0	0	0	0	0	1	1	1
Total Suspended Solids	1	1	1	0	0	0	0	0	0	1	1	1
Ammonia as N	1	1	1	1	1	1	0	0	0	2	2	2
Total Residual Chlorine	0	1	1	0	0	0	0	0	0	0	1	1
Total Kjeldhal Nitrogen	1	1	1	1	1	1	0	0	0	2	2	2
Nitrate plus Nitrite Nitrogen	1	1	1	1	1	1	0	0	0	2	2	2
Oil and Grease	1	1	1	0	0	0	0	0	0	1	1	1
Total Phosphorus	1	1	1	1	1	1	0	0	0	2	2	2
Total Dissolved Solids	1	1	1	0	0	0	0	0	0	1	1	1
Turbidity (NTU)	1	1	1	0	0	0	0	0	0	1	1	1
Metals	1	1	1	1	1	1	2[3]	2[3]	2[3]	4	4	4
Cyanide	1	1	1	0	0	0	1[6]	0	0	2	1	1
Total Phenolic Compounds	1	1	1	0	0	0	1[6]	0	0	2	1	1
Volatile Organic Compounds	1	1	1	0	0	0	1[6]	0	0	2	1	1
Acid Extactable Compounds	1	1	1	0	0	0	1[6]	0	0	2	1	1
Base-Neutral Compounds	1	1	1	0	0	0	1[6]	0	0	2	1	1

Field Parameters	Second Sample Round											
	Total Sampling Frequency			No. Field Replicates[1]			No of Other QC Samples[2]			Total No. of Samples in Field		
	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington
Dissolved Oxygen	1	1	1	1	1	1	0	0	0	2	2	2
pH	1	1	1	1	1	1	0	0	0	2	2	2
Conductivity	1	1	1	1	1	1	0	0	0	2	2	2
Temperature	1	1	1	1	1	1	0	0	0	2	2	2

[1] - Includes Field Duplicates for Laboratory Samples and Field Replicates for Field Samples (In-situ)

[2] - Includes Trip Blanks (T), Equipment blanks (E), and Matrix Spike/Matrix Spike Duplicates(S)

[3] - Includes Equipment blank (E), and Matrix Spike/Matrix Spike Duplicates(S)

[4] - Includes Trip Blank (T) and Equipment blank (E)

[5] - Includes Equipment blank (E)

[6] - Includes Trip blank (T)

Laboratory Parameters	Third Sample Round											
	Total Sampling Frequency			No. of Field Duplicates[1]			No of Other QC Samples [2]			Total No. of Samples to Laboratory		
	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington
Biochemical Oxygen Demand	1	1	1	0	0	0	0	0	0	1	1	1
Enterococci	1	1	1	0	0	0	0	0	0	1	1	1
Fecal Coliform	1	1	1	0	0	0	0	0	0	1	1	1
Total Suspended Solids	1	1	1	0	0	0	0	0	0	1	1	1
Ammonia as N	1	1	1	1	1	1	0	0	0	2	2	2
Total Residual Chlorine	0	1	1	0	0	0	0	0	0	0	1	1
Total Kjeldhal Nitrogen	1	1	1	1	1	1	0	0	0	2	2	2
Nitrate plus Nitrite Nitrogen	1	1	1	1	1	1	0	0	0	2	2	2
Oil and Grease	1	1	1	0	0	0	0	0	0	1	1	1
Total Phosphorus	1	1	1	1	1	1	0	0	0	2	2	2
Total Dissolved Solids	1	1	1	0	0	0	0	0	0	1	1	1
Turbidity (NTU)	1	1	1	0	0	0	0	0	0	1	1	1
Metals	1	1	1	1	1	1	2 [3]	2 [3]	2 [3]	4	4	4
Cyanide	1	1	1	0	0	0	1 [6]	0	0	2	1	1
Total Phenolic Compounds	1	1	1	0	0	0	1 [6]	0	0	2	1	1
Volatile Organic Compounds	1	1	1	0	0	0	1 [6]	0	0	2	1	1
Acid Extactable Compounds	1	1	1	0	0	0	1 [6]	0	0	2	1	1
Base-Neutral Compounds	1	1	1	0	0	0	1 [6]	0	0	2	1	1

Field Parameters	Third Sample Round											
	Total Sampling Frequency			No. Field Replicates [1]			No of Other QC Samples [2]			Total No. of Samples in Field		
	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington
Dissolved Oxygen	1	1	1	1	1	1	0	0	0	2	2	2
pH	1	1	1	1	1	1	0	0	0	2	2	2
Conductivity	1	1	1	1	1	1	0	0	0	2	2	2
Temperature	1	1	1	1	1	1	0	0	0	2	2	2

[1] - Includes Field Duplicates for Laboratory Samples and Field Replicates for Field Samples (In-situ)

[2] - Includes Trip Blanks (T), Equipment blanks (E), and Matrix Spike/Matrix Spike Duplicates(S)

[3] - Includes Equipment blank (E), and Matrix Spike/Matrix Spike Duplicates(S)

[4] - Includes Trip Blank (T) and Equipment blank (E)

[5] - Includes Equipment blank (E)

[6] - Includes Trip blank (T)

Laboratory Parameters	Fourth Sample Round											
	Total Sampling Frequency			No. of Field Duplicates[1]			No of Other QC Samples [2]			Total No. of Samples to Laboratory		
	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington
Biochemical Oxygen Demand	1	1	1	0	0	0	0	0	0	1	1	1
Enterococci	1	1	1	0	0	0	0	0	0	1	1	1
Fecal Coliform	1	1	1	0	0	0	0	0	0	1	1	1
Total Suspended Solids	1	1	1	0	0	0	0	0	0	1	1	1
Ammonia as N	1	1	1	1	1	1	0	0	0	2	2	2
Total Residual Chlorine	0	1	1	0	0	0	0	0	0	0	1	1
Total Kjeldhal Nitrogen	1	1	1	1	1	1	0	0	0	2	2	2
Nitrate plus Nitrite Nitrogen	1	1	1	1	1	1	0	0	0	2	2	2
Oil and Grease	1	1	1	0	0	0	0	0	0	1	1	1
Total Phosphorus	1	1	1	1	1	1	0	0	0	2	2	2
Total Dissolved Solids	1	1	1	0	0	0	0	0	0	1	1	1
Turbidity (NTU)	1	1	1	0	0	0	0	0	0	1	1	1
Metals	1	1	1	1	1	1	2 [3]	2 [3]	2 [3]	4	4	4
Cyanide	1	1	1	0	0	0	1 [6]	0	0	2	1	1
Total Phenolic Compounds	1	1	1	0	0	0	1 [6]	0	0	2	1	1
Volatile Organic Compounds	1	1	1	0	0	0	1 [6]	0	0	2	1	1
Acid Extactable Compounds	1	1	1	0	0	0	1 [6]	0	0	2	1	1
Base-Neutral Compounds	1	1	1	0	0	0	1 [6]	0	0	2	1	1

Field Parameters	Fourth Sample Round											
	Total Sampling Frequency			No. Field Replicates [1]			No of Other QC Samples [2]			Total No. of Samples in Field		
	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington
Dissolved Oxygen	1	1	1	1	1	1	0	0	0	2	2	2
pH	1	1	1	1	1	1	0	0	0	2	2	2
Conductivity	1	1	1	1	1	1	0	0	0	2	2	2
Temperature	1	1	1	1	1	1	0	0	0	2	2	2

[1] - Includes Field Duplicates for Laboratory Samples and Field Replicates for Field Samples (In-situ)

[2] - Includes Trip Blanks (T), Equipment blanks (E), and Matrix Spike/Matrix Spike Duplicates(S)

[3] - Includes Equipment blank (E), and Matrix Spike/Matrix Spike Duplicates(S)

[4] - Includes Trip Blank (T) and Equipment blank (E)

[5] - Includes Equipment blank (E)

[6] - Includes Trip blank (T)

Laboratory Parameters	Project Total Sample Count												
	Total Sampling Frequency			No. of Field Duplicates[1]			No of Other QC Samples [2]			Total No. of Samples to Laboratory			
	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	**Total**
Biochemical Oxygen Demand	4	4	4	1	1	1	0	0	0	5	5	5	**15**
Enterococci	4	4	4	1	1	1	0	0	0	5	5	5	**15**
Fecal Coliform	4	4	4	1	1	1	0	0	0	5	5	5	**15**
Total Suspended Solids	4	4	4	1	1	1	0	0	0	5	5	5	**15**
Ammonia as N	4	4	4	4	4	4	0	0	0	8	8	8	**24**
Total Residual Chlorine	0	4	4	0	1	1	0	0	0	0	5	5	**10**
Total Kjeldhal Nitrogen	4	4	4	4	4	4	0	0	0	8	8	8	**24**
Nitrate plus Nitrite Nitrogen	4	4	4	4	4	4	0	0	0	8	8	8	**24**
Oil and Grease	4	4	4	1	1	1	0	0	0	5	5	5	**15**
Total Phosphorus	4	4	4	4	4	4	0	0	0	8	8	8	**24**
Total Dissolved Solids	4	4	4	1	1	1	0	0	0	5	5	5	**15**
Turbidity (NTU)	4	4	4	1	1	1	0	0	0	5	5	5	**15**
Metals	4	4	4	4	4	4	8	8	8	16	16	16	**48**
Seawater	4			4			8			16	0	0	**16**
WWTF		4	4		4	4		8	8	0	16	16	**32**
Cyanide	4	4	4	1	1	1	5	1	1	10	6	6	**22**
Total Phenolic Compounds	4	4	4	1	1	1	5	1	1	10	6	6	**22**
Volatile Organic Compounds	4	4	4	1	1	1	5	1	1	10	6	6	**22**
Acid Extactable Compounds	4	4	4	1	1	1	5	1	1	10	6	6	**22**
Base-Neutral Compounds	4	4	4	1	1	1	5	1	1	10	6	6	**22**

Field Parameters	Project Total Sample Count												
	Total Sampling Frequency			No. Field Replicates [1]			No of Other QC Samples [2]			Total No. of Samples in Field			
	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	River	WWTF Pease	WWTF Newington	**Total**
Dissolved Oxygen	4	4	4	4	4	4	0	0	0	8	8	8	**24**
pH	4	4	4	4	4	4	0	0	0	8	8	8	**24**
Conductivity	4	4	4	4	4	4	0	0	0	8	8	8	**24**
Temperature	4	4	4	4	4	4	0	0	0	8	8	8	**24**

[1] - Includes Field Duplicates for Laboratory Samples and Field Replicates for Field Samples (In-situ)

[2] - Includes Trip Blanks (T), Equipment blanks (E), and Matrix Spike/Matrix Spike Duplicates(S)

[3] - Includes Equipment blank (E), and Matrix Spike/Matrix Spike Duplicates(S)

[4] - Includes Trip Blank (T) and Equipment blank (E)

[5] - Includes Equipment blank (E)

APPENDIX C

Standard of Practice for Grab Sampling

SOP for Grab Sampling

Modified from: "Ambient River Monitoring Program Standard Operating Procedures (SOP) Sampling, Custody, and Laboratory Login", Revision 3: April 20, 2006", NH Department of Environmental Services

Sample Bottle/Field Measurement by Boat

Step 1. Don a PFD. Staff will wear disposable latex or nitrile gloves during sample collection.

Step 2. Propel the boat in a downstream to upstream direction when approaching the sampling area. If access is required from upstream, propel the boat or float with the current along the stream margins being careful not to agitate the water in the thalweg or center of the stream. If a thalweg is not apparent, propel the boat into the center of the channel. Stop the boat and drop the anchor as necessary. Wait 3-5 minutes for water to flow past the boat.

Step 3. Position the opening of the sample bottle at an arm's length from the boat gunwale on the upstream side of the boat, completely fill the bottle, and tighten the cap.
NOTE: Do not fill the sample bottle with water that has contacted the boat.
NOTE: If required for metals analyses, filter sample prior to pouring into sample bottle.

Step 4. Place all filled water sample bottles on ice in the cooler as soon as possible after collection and ensure the top of the cooler is tightly closed.

Step 5. Record all field notes, including station ID, date, time, field measurement results, etc. on the field data sheets.

Bacteria Sampling

The following is additional information for collecting samples for bacteria analyses.

1. Bacteria samples will be collected directly in plastic sterile bottles provided by analytical laboratory.
2. In an effort to obtain a representative sample staff will try not to disturb the channel bottom while sampling.

3. Remove the cap of a sterilized bottle when ready to collect the sample. Avoid touching the inside the bottle or cap to prevent contamination.

4. The samples will be collected by plunging the mouth of the bottle through the surface of the water. Position the bottle so that the mouth is going up the channel about 6-12 inches below the surface. If the water does not have a current, move the bottle horizontally in the direction so that it is pointed away from the sampler. Tip the bottle slightly upward to allow the air to exit and the bottle to fill. After removing the bottle from the water pour out a small portion of the sample so that a small air space will remain. Then recap the bottle.

5. After the bacteria sample has been collected it will be put on ice and remain chilled until it has reached the laboratory. Care will be taken not to freeze the samples. Any samples with ice present will be rejected and another sample will be collected.

APPENDIX D

Standard Operating Procedure for Collection of Water Quality Data with Multi-Parameter Water Quality Meter

Standard Operating Procedure for Collection of Water Quality Data using MultiParameter Water Quality Meter

Step 1. Don a PFD.

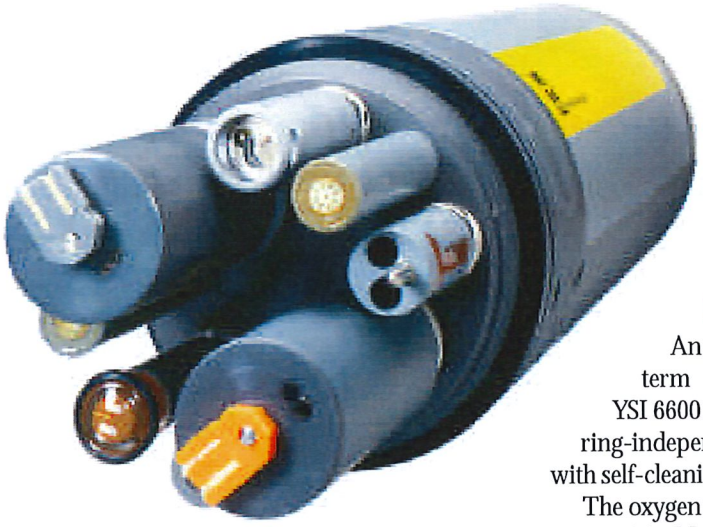
Step 2. Propel the boat in a downstream to upstream direction when approaching the sampling area. If access is required from upstream, propel the boat or float with the current along the stream margins being careful not to agitate the water in the thalweg or center of the stream. If a thalweg is not apparent, propel the boat into the center of the channel. Stop the boat and drop the anchor as necessary. Connect water quality meter cable to anchoring cable with carabineers to prevent horizontal drifting. Wait 3-5 minutes for water to flow past the boat.

Step 3. Lower the water quality probe to approximately 0.5 meter below the water surface. Allow readings on meter to stabilize and then record parameters (dissolved oxygen, pH, temperature, conductivity, and salinity) on field data sheets or notebook. Collect field replicate values and record on field data sheets or notebook.

YSI Environmental

YSI 6600 Sonde

Featuring 75-day battery life — the longest in the industry — the YSI 6600 has a second optical port to enable simultaneous use of self-cleaning chlorophyll or rhodamine and turbidity. It will simultaneously log at programmable intervals the entire suite of YSI parameters and store 150,000 individual parameter readings.



- 75-day battery life
- Deep depth to 656 feet
- Two optical ports for self-cleaning turbidity and chlorophyll or rhodamine probes
- Open-channel flow

Long Deployment

An important advantage of the YSI 6600 is the capability for long-term monitoring and profiling. In addition to long battery life, the YSI 6600 measures dissolved oxygen with YSI's exclusive Rapid Pulse™ stirring-independent sensor. Chlorophyll, rhodamine, and turbidity are measured with self-cleaning sensors that are not affected by variations in ambient light.

The oxygen sensor measures up to 50 mg/L, broad enough for super-saturated water. YSI's chlorophyll sensor provides a convenient, *in situ* monitoring system for detecting chlorophyll content in phytoplankton, which can be used to predict algae blooms and nutrient loading in water. The rhodamine sensor allows for time-of-travel and mixing/dispersion zone studies while logging water quality parameters.

Easy-to-Use Data Analysis

Included with the YSI 6600 is EcoWatch® for Windows® software, providing user-friendly data analysis and statistics. This exclusive YSI tool is in English and French, as is the instrument's software.

Pure Data for a Healthy Planet.™

More Power and More Parameters for Long-Term Monitoring and Profiling!

Instrument Specifications	
Medium	Fresh, sea, or polluted water
Temperature	-5 to +45°C
Computer interface	RS-232, SDI-12
Logging memory	384K; logs at programmable intervals and stores 150,000 readings
Software	EcoWatch for Windows included: PC-compatible, 3.5" disk drive; 386 processor or better running Windows 3.1 or later; 4 MB RAM minimum; English and French.
Size	3.5" OD x 20.4" length (8.9 x 52 cm)
Weight with batteries :	6 lbs (2.7 kg)
Internal power supply	8 C alkaline cells
Battery life	75 days at 15-minute sampling intervals at 25°C
External power supply	12 VDC

YSI Environmental

Pure Data for a Healthy Planet.™

To order or for more information, contact YSI Environmental.

800 897-4151

www.YSI.com

YSI Environmental
937 767 7241
Fax 937 767 9353
environmental@YSI.com

Endeco/YSI
508 748 0366
Fax 508 748 2543
environmental@YSI.com

YSI Environmental
European Support Centre
44 1730 710 615
Fax 44 1730 710 614
europe@YSI.com

YSI (Hong Kong) Limited
852 2891 8154
Fax 852 2834 0034
hongkong@YSI.com

YSI/Nanotech (Japan)
81 44 222 0009
Fax 81 44 222 1102
nanotech@YSI.com

YSI (Qingdao) Limited
86 532 389 6648
Fax 86 532 389 6647
china@YSI.com

ISO 9001
ISO 14001

Printed in USA 0103 E33-02

CE

YSI incorporated
Who's Minding the Planet?™

Typical Performance Specifications

Dissolved Oxygen % Saturation	Range Resolution Accuracy	0 to 500% 0.1% 0 to 200%: ±2% of reading or 2% air saturation, whichever is greater; 200 to 500%: ±6% of reading
Dissolved Oxygen mg/L	Range Resolution Accuracy	0 to 50 mg/L 0.01 mg/L 0 to 20 mg/L: ±2% of reading or 0.2 mg/L, whichever is greater; 20 to 50 mg/L: ±6% of reading
Conductivity †	Range Resolution Accuracy	0 to 100 mS/cm 0.001 to 0.1 mS/cm (range-dependent) ±0.5% of reading + 0.001 mS/cm
Temperature	Range Resolution Accuracy	-5 to +45°C 0.01°C ±0.15°C
pH	Range Resolution Accuracy	0 to 14 units 0.01 unit ±0.2 unit
ORP	Range Resolution Accuracy	-999 to +999 mV 0.1 mV ±20 mV
Salinity	Range Resolution Accuracy	0 to 70 ppt 0.01 ppt ±1% of reading or 0.1 ppt, whichever is greater
Shallow Depth	Range Resolution Accuracy	0 to 30 feet (0 to 9 m) 0.001 feet (0.001 m) ±0.06 feet (±0.02 m)
Medium Depth	Range Resolution Accuracy	0 to 200 feet (0 to 61 m) 0.001 feet (0.001 m) ±0.4 feet (±0.12 m)
Deep Depth	Range Resolution Accuracy	0 to 656 feet (0 to 200 m) 0.001 feet (0.001 m) ±1 feet (±0.3 m)
Vented Level	Range Resolution Accuracy	0 to 30 feet (0 to 9 m) 0.001 feet (0.0003 m) ±0.01 feet (0.003 m)
Turbidity	Range Resolution Accuracy Depth	0 to 1,000 NTU 0.1 NTU ±5% of reading or 2 NTU, whichever is greater 200 feet (60.96 m)
Chlorophyll	Range Resolution Depth	0 to 400 µg/L 0.1 µg/L Chl; 0.1%FS 200 feet (60.96 m)
Rhodamine	Range Resolution Accuracy Depth	0 to 200 µg/L; 0 to 100% FS 0.1 µg/L; 0.1% FS ±1.0 µg/L; 5% of reading 200 feet (60.96 m)
Ammonium/ Ammonia*	Range Resolution Accuracy Depth	0 to 200 mg/L-N 0.001 to 1 mg/L-N (range-dependent) ±10% of reading or 2 mg/L, whichever is greater 50 feet (15.2 m)
Nitrate *	Range Resolution Accuracy Depth	0 to 200 mg/L-N 0.001 to 1 mg/L-N (range-dependent) ±10% of reading or 2 mg/L, whichever is greater 50 feet (15.2 m)
Chloride *	Range Resolution Accuracy Depth	0 to 1,000 mg/L 0.001 to 1 mg/L (range-dependent) ±15% of reading or 5 mg/L, whichever is greater 200 feet (60.96 m)
Open-Channel Flow	Calculated measurement, requires vented level	

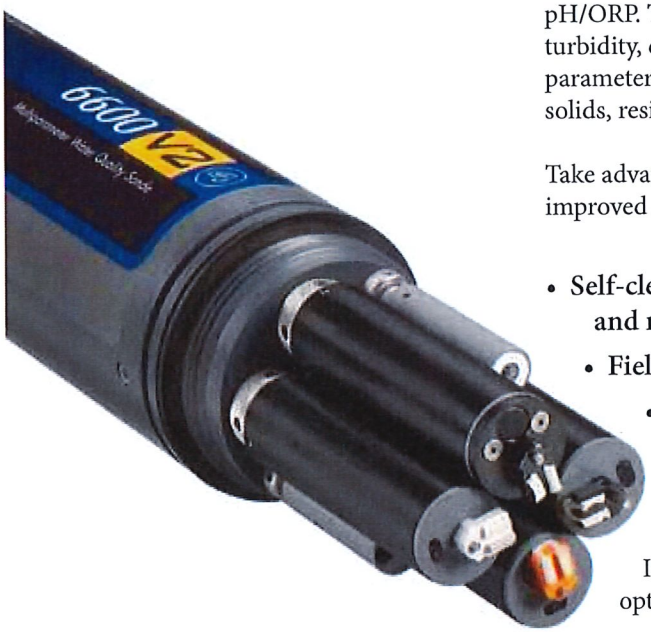
† Report outputs of specific conductance (conductivity corrected to 25° C), resistivity, and total dissolved solids are also provided. These values are automatically calculated from conductivity according to algorithms found in *Standard Methods for the Examination of Water and Wastewater* (ed 1989).

YSI Environmental

YSI 6600 V2 Sonde

With 2 or 4 optical ports and new sensor options

Make the most of your environmental monitoring efforts: The 6600 V2 sonde offers the most comprehensive water quality monitoring package available with simultaneous measurement of conductivity (salinity), temperature, depth or level, pH/ORP. The 6600 V2-4 also measures these parameters: dissolved oxygen, turbidity, chlorophyll, and blue-green algae; the V2-2 measures two of the four parameters simultaneously. Additional calculated parameters include total dissolved solids, resistivity, and specific conductance.



Take advantage of YSI's new optical sensor design and anti-fouling wiper control for improved reliability during extended deployments.

- **Self-cleaning optical sensors with integrated wipers remove biofouling and maintain high data accuracy**
- **Field-replaceable sensors make trips to the field quick**
- **Optimal power management and built-in battery compartment extends *in situ* monitoring periods**

Take Advantage of YSI's New Optical Sensors

In addition to turbidity, chlorophyll, and rhodamine, YSI now offers these optical sensors:

Complete Data Record

The YSI 6600 V2-4 Sonde, with 4 optical sensor ports, is the only instrument available to simultaneously measure dissolved oxygen, turbidity, chlorophyll, and blue-green algae!

ROX Reliable Optical Dissolved Oxygen

The ROX sensor uses lifetime luminescence detection technology to offer the most reliable oxygen sensor with the lowest possible maintenance effort. The sensor is insensitive to hydrogen sulfide interference and does not require regular membrane changes.

Blue-Green Algae (BGA)

YSI's fluorescence-based blue-green algae sensors will allow you to monitor blue-green algae populations where their presence is a concern. Whether providing an early warning to an algal bloom, tracking taste and odor-causing species in drinking water supplies, or conducting ecosystem research, YSI BGA sensors will provide sensitive and reliable *in situ* data.

Pure Data for a Healthy Planet.®

Upgraded sondes for rugged long-term deployment

*Sensor performance verified**

The 6600 V2 sonde uses sensor technology that was verified through the US EPA's Environmental Technology Verification Program (ETV). For information on which sensors were performance-verified, turn this sheet over and look for the ETV logo.

6600 Upgrades Available

YSI is committed to offering our customers reliable and cost-effective water monitoring solutions. To this end, we are offering V2 Upgrades for existing 6600s. Upgrades will be available from YSI Authorized Service Centers and will include the new 6600 V2 bulkhead, a ROX Optical Dissolved Oxygen Sensor, and firmware/software upgrades. In addition, the sonde will be fully tested and calibrated by an experienced YSI service technician.

www.ysi.com/v2

YSI 6600 V2 Sensor Specifications

	Range	Resolution	Accuracy
ROX™ Optical Dissolved Oxygen• % Saturation	0 to 500%	0.1%	0 to 200%: ±1% of reading or 1% air saturation, whichever is greater; 200 to 500%: ±15% of reading
ROX™ Optical Dissolved Oxygen• mg/L	0 to 50 mg/L	0.01 mg/L	0 to 20 mg/L: ± 0.1 mg/L or 1% of reading, whichever is greater; 20 to 50 mg/L: ±15% of reading
Dissolved Oxygen•• % Saturation ETV 6562 Rapid Pulse™ Sensor*	0 to 500%	0.1%	0 to 200%: ±2% of reading or 2% air saturation, whichever is greater; 200 to 500%: ±6% of reading
Dissolved Oxygen•• mg/L ETV 6562 Rapid Pulse™ Sensor*	0 to 50 mg/L	0.01 mg/L	0 to 20 mg/L: ± 0.2 mg/L or 2% of reading, whichever is greater; 20 to 50 mg/L: ±6% of reading
Conductivity••• ETV 6560 Sensor*	0 to 100 mS/cm	0.001 to 0.1 mS/cm (range dependent)	±0.5% of reading + 0.001 mS/cm
Salinity	0 to 70 ppt	0.01 ppt	±1% of reading or 0.1 ppt, whichever is greater
Temperature ETV 6560 Sensor*	-5 to +50°C	0.01°C	±0.15°C
pH ETV 6561 Sensor*	0 to 14 units	0.01 unit	±0.2 unit
ORP	-999 to +999 mV	0.1 mV	±20 mV
Depth Deep	0 to 656 ft, 200 m	0.001 ft, 0.001 m	±1 ft, ±0.3 m
Depth Medium	0 to 200 ft, 61 m	0.001 ft, 0.001 m	±0.4 ft, ±0.12 m
Depth Shallow	0 to 30 ft, 9.1 m	0.001 ft, 0.001 m	±0.06 ft, ±0.02 m
Depth Vented Level	0 to 30 ft, 9.1 m	0.001 ft, 0.001 m	±0.01 ft, 0.003 m
Turbidity• ETV 6136 Sensor*	0 to 1,000 NTU	0.1 NTU	±2% of reading or 0.3 NTU, whichever is greater••
Nitrate/nitrogen••••	0 to 200 mg/L-N	0.001 to 1 mg/L-N (range dependent)	±10% of reading or 2 mg/L, whichever is greater
Ammonium/ammonia/ nitrogen••••	0 to 200 mg/L-N	0.001 to 1 mg/L-N (range dependent)	±10% of reading or 2 mg/L, whichever is greater
Chloride••••	0 to 1000 mg/L	0.001 to 1 mg/L (range dependent)	±15% of reading or 5 mg/L, whichever is greater
Rhodamine•	0-200 µg/L	0.1 µg/L	±5% reading or 1 µg/L, whichever is greater

• Maximum depth rating for all optical probes is 200 feet, 61 m. Turbidity and Rhodamine are also available in a Deep Depth option (0 to 200 m).
•• Rapid Pulse is only available on 6600 V2-2 (two optical ports version).
••• Report outputs of specific conductance (conductivity corrected to 25° C), resistivity, and total dissolved solids are also provided. These values are automatically calculated from conductivity according to algorithms found in *Standard Methods for the Examination of Water and Wastewater* (ed 1989).
•••• Freshwater only. Maximum depth rating of 50 feet, 15.2 m. 6600 V2-2 has 3 ISE ports; not available on the 6600V2-4.

**In YSI AMCO-AEPA Polymer Standards.

	Range	Detection Limit	Resolution	Linearity
Blue-Green Algae Phycocyanin•	~0 to 280,000 cells/mL† 0 to 100 RFU	~220 cells/mL§	1 cell/mL 0.1 RFU	$R^2 > 0.9999$**
Blue-Green Algae Phycoerythrin•	~0 to 200,000 cells/mL† 0 to 100 RFU	~450 cells/mL§§	1 cell/mL 0.1 RFU	$R^2 > 0.9999$***
Chlorophyll• ETV 6025 Sensor*	~0 to 400 µg/L 0 to 100 RFU	~0.1 µg/L§§§	0.1 µg/L Chl 0.1% RFU	$R^2 > 0.9999$****

• Maximum depth rating for all optical probes is 200 feet, 61 m. Also available in a Deep Depth option (0 to 200 m).
RFU = Relative Fluorescence Units

† Explanation of Ranges can be found in the 'Principles of Operation' section of the 6-Series Manual, Rev D.

§ Estimated from cultures of *Microcystis aeruginosa*.
§§ Estimated from cultures *Synechococcus sp.*
§§§ Determined from cultures of *Isochrysis sp.* and chlorophyll *a* concentration determined via extractions.

**For serial dilution of Rhodamine WT (0-400 ug/L).
***For serial dilution of Rhodamine WT (0-8 µg/L).
****For serial dilution of Rhodamine WT (0-500 ug/L).

YSI 6600 V2 Sonde Specifications

Medium	Fresh, sea or polluted water	Software		EcoWatch®
Temperature	Operating	-5 to +50°C	Dimensions Diameter	3.5 in, 8.9 cm
	Storage	-10 to +60°C	Length, no depth	19.6 in, 49.8 cm
			Length, with depth	21.6 in, 54.9 cm
			Weight	7 lbs, 3.18 kg (batteries installed, with depth)
Communications	RS-232, SDI-12	Power	External	12 V DC
			Internal	8 C-size alkaline batteries

To order, or for more info, contact YSI Environmental.

+1 937 767 7241
800 897 4151 (US)
www.ysi.com

YSI Environmental
+1 937 767 7241
Fax +1 937 767 9353
environmental@ysi.com

YSI Integrated Systems & Services
+1 508 748 0366
systems@ysi.com

SonTek/YSI
+1 858 546 8327
inquiry@sontek.com

YSI Gulf Coast
+1 225 753 2650
gulfcoast@ysi.com

YSI Hydrodata (UK)
+44 1462 673 581
europe@ysi.com

YSI Middle East (Bahrain)
+973 39771055
halsalem@ysi.com

YSI South Asia
+91 124 435 4213
sham@ysi.com

YSI Hong Kong
+852 2891 8154
hongkong@ysi.com

YSI China
+86 10 8571 1975
beijing@ysi-china.com

YSI Nanotech (Japan)
+81 44 222 0009
nanotech@ysi.com

YSI Australia
+61 7 3162 1064
australia@ysi.com

ISO 9001
ISO 14001
Yellow Springs, Ohio Facility

Printed in USA 1110 E52-02

CE

*Sensors with listed with ETV logo were submitted to the ETV program on the YSI 6600EDS. Information on performance characteristics of YSI water quality sensors can be found at www.epa.gov/etv, or call YSI at 800.897.4151 for the ETV verification report. Use of ETV name or logo does not imply approval or certification of this product nor does it make any explicit or implied warranties or guarantees as to product performance.

YSI incorporated
Who's Minding the Planet?®

APPENDIX E

U.S. Environmental Protection Agency

Method 1669

Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels

Method 1669

Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels

July 1996

U.S. Environmental Protection Agency
Office of Water
Engineering and Analysis Division (4303)
401 M Street S.W.
Washington, D.C. 20460

Introduction

This sampling method was designed to support water quality monitoring programs authorized under the Clean Water Act. Section 304(a) of the Clean Water Act requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability.

Section 303 of the Clean Water Act requires states to set a water quality standard for each body of water within its boundaries. A state water quality standard consists of a designated use or uses of a waterbody or a segment of a waterbody, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by Sections 301(b) and 306 of the Clean Water Act.

In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to the Clean Water Act required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and required to support technology-based permits. Therefore, this sampling method, and the analytical methods referenced in Table 1 of this document, were developed by EPA to specifically address state needs for measuring toxic metals at water quality criteria levels, when such measurements are necessary to protect designated uses in state water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (57 *FR* 60848) and the Stay of Federal Water Quality Criteria for Metals (60 *FR* 22228). These rules include water quality criteria for 13 metals, and it is these criteria on which this sampling method and the referenced analytical methods are based.

In developing these methods, EPA found that one of the greatest difficulties in measuring pollutants at these levels was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This method, therefore, is designed to provide the level of protection necessary to preclude contamination in nearly all situations. It is also designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, the method is performance-based. Alternative procedures may be used, so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies of this method should be directed to:

U.S. EPA NCEPI
11029 Kenwood Road
Cincinnati, OH 45242
513/489–8190

Method 1669

Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels

1.0 Scope and Application

1.1 This method is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved metals at the levels listed in Table 1. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act.

1.2 This method is applicable to the metals listed below and other metals, metals species, and elements amenable to determination at trace levels.

Analyte	Symbol	Chemical Abstract Services Registry Number (CASRN)
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Cadmium	(Cd)	7440-43-9
Chromium (III)	Cr^{+3}	16065-83-1
Chromium (VI)	Cr^{+6}	18540-29-9
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Zinc	(Zn)	7440-66-6

1.3 This method is accompanied by the 1600 series methods listed in Table 1. These methods include the sample handling, analysis, and quality control procedures necessary for reliable determination of trace metals in aqueous samples.

1.4 This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 *CFR* Parts 400-500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range. This guidance is therefore directed at the collection of samples to be measured at or near the levels listed in Table 1. Actual concentration ranges to which this guidance is applicable will be dependent on the sample matrix, dilution levels, and other laboratory operating conditions.

1.5 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination. These techniques are given in Section 8.0 and are based on findings of researchers performing trace metals analyses (References 1-9).

one field blank should be processed per site, or one per every ten samples, whichever is more frequent (Section 9.4). If samples are to be collected for determination of trivalent chromium, the sampling team processes additional QC aliquots are processed as described in Section 9.6.

2.4 Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is responsible for preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample.

2.5 All sampling equipment and sample containers used for metals determinations at or near the levels listed in Table 1 must be nonmetallic and free from any material that may contain metals.

2.6 Sampling personnel are required to wear clean, nontalc gloves at all times when handling sampling equipment and sample containers.

2.7 In addition to processing field blanks at each site, a field duplicate must be collected at each sampling site, or one field duplicate per every 10 samples, whichever is more frequent (Section 9.5). Section 9.0 gives a complete description of quality control requirements.

2.8 Sampling

2.8.1 Whenever possible, samples are collected facing upstream and upwind to minimize introduction of contamination.

2.8.2 Samples may be collected while working from a boat or while on land.

2.8.3 Surface samples are collected using a grab sampling technique. The principle of the grab technique is to fill a sample bottle by rapid immersion in water and capping to minimize exposure to airborne particulate matter.

2.8.4 Subsurface samples are collected by suction of the sample into an immersed sample bottle or by pumping the sample to the surface.

2.9 Samples for dissolved metals are filtered through a 0.45 µm capsule filter at the field site. After filtering, the samples are double-bagged and iced immediately. Sample containers are shipped to the analytical laboratory. The sampling equipment is shipped to the laboratory or cleaning facility for recleaning.

2.10 Acid preservation of samples is performed in the field or in the laboratory. Field preservation is necessary for determinations of trivalent chromium. It has also been shown that field preservation can increase sample holding times for hexavalent chromium to 30 days; therefore it is recommended that preservation of samples for hexavalent chromium be performed in the field. For other metals, however, the sampling team may prefer to utilize laboratory preservation of samples to expedite field operations and to minimize the potential for sample contamination.

Apparatus are given in this sampling method and in the methods referenced in Table 1.

4.2.1.3 While contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in Section 5 of this sampling method and in the methods referenced in Table 1.

4.2.2 Avoiding contamination—The best way to control contamination is to completely avoid exposure of the sample and Apparatus to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being performed. Therefore, it is imperative that the procedures described in this method be carried out by well trained, experienced personnel. Documentation of training should be kept on file and readily available for review.

4.2.2.1 Minimize exposure—The Apparatus that will contact samples or blanks should only be opened or exposed in a clean room, clean bench, glove box, or clean plastic bag, so that exposure to atmospheric inputs is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean, colorless zip-type bags. Minimizing the time between cleaning and use will also reduce contamination.

4.2.2.2 Wear gloves—Sampling personnel must wear clean, nontalc gloves (Section 6.7) during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.2.2.3 Use metal-free Apparatus—All Apparatus used for metals determinations at the levels listed in Table 1 must be nonmetallic and free of material that may contain metals. When it is not possible to obtain equipment that is completely free of the metal(s) of interest, the sample should not come into direct contact with the equipment.

4.2.2.3.1 Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polysulfone, polypropylene, or ultrapure quartz. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminants and is susceptible to serious memory effects (Reference 6). Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse

highest levels collected last (Section 8.1.4). This will help minimize carryover of metals from high- concentration samples to low- concentration samples. If the sampling team does not have prior knowledge of the waterbody, or when necessary, the sample collection system should be rinsed with dilute acid and reagent water between samples and followed by collection of a field blank (Section 10.3).

4.2.2.4.2 Contamination by samples—Significant contamination of the Apparatus may result when untreated effluents, in-process waters, landfill leachates, and other samples containing mid- to high-level concentrations of inorganic substances are processed. As stated in Section 1.0, this sampling method is not intended for application to these samples, and samples containing high concentrations of metals must not be collected, processed, or shipped at the same time as samples being collected for trace metals determinations.

4.2.2.4.3 Contamination by indirect contact—Apparatus that may not directly contact samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in the collection of ambient water samples be cleaned as specified in the analytical method(s) referenced in Table 1.

4.2.2.4.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particulate matter, or vapors from automobile exhaust; cigarette smoke; nearby corroded or rusted bridges, pipes, poles, or wires; nearby roads; and even human breath (Section 4.1.2). Whenever possible, the sampling activity should occur as far as possible from sources of airborne contamination (Section 8.1.3). Areas where nearby soil is bare and subject to wind erosion should be avoided.

4.3 Interferences—Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled. If a sample is suspected of containing substances that may interfere in the determination of trace metals, sufficient sample should be collected to allow the laboratory to identify and overcome interference problems.

5.0 Safety

5.1 The toxicity or carcinogenicity of the chemicals used in this method has not been precisely determined; however, these chemicals should be treated as a potential health

adsorb or contribute mercury must be used if mercury is a target analyte; otherwise, polyethylene, polycarbonate, or polypropylene are acceptable. Commercially available sampling devices may be used provided that any metallic or metal-containing parts are replaced with parts constructed of nonmetallic material.

6.4 Surface Sampling Devices—Surface samples are collected using a grab sampling technique. Samples may be collected manually by direct submersion of the bottle into the water or by using a grab sampling device. Examples of grab samplers are shown in Figures 1 and 2 and may be used at sites where depth profiling is neither practical nor necessary.

6.4.1 The grab sampler in Figure 1 consists of a heavy fluoropolymer collar fastened to the end of a 2-m-long polyethylene pole, which serves to remove the sampling personnel from the immediate vicinity of the sampling point. The collar holds the sample bottle. A fluoropolymer closing mechanism, threaded onto the bottle, enables the sampler to open and close the bottle under water, thereby avoiding surface microlayer contamination (Reference 14). Polyethylene, polycarbonate, and polypropylene are also acceptable construction materials unless mercury is a target analyte. Assembly of the cleaned sampling device is as follows (refer to Figure 1):

6.4.1.1 Thread the pull cord (with the closing mechanism attached) through the guides and secure the pull ring with a simple knot. Screw a sample bottle onto the closing device and insert the bottle into the collar. Cock the closing plate so that the plate is pushed away from the operator.

6.4.1.2 The cleaned and assembled sampling device should be stored in a double layer of large, clean zip-type polyethylene bags or wrapped in two layers of clean polyethylene wrap if it will not be used immediately.

6.4.2 An alternate grab sampler design is shown in Figure 2. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be submerged, the cap removed, sample collected, and bottle recapped at a selected depth. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination. Because a fresh bottle is used for each sample, carryover from previous samples is eliminated (Reference 15).

6.5 Subsurface Sampling Devices—Subsurface sample collection may be appropriate in lakes and sluggish deep river environments or where depth profiling is determined to be necessary. Subsurface samples are collected by pumping the sample into a sample bottle. Examples of subsurface collection systems include the jar system device shown in Figure 3 and described in Section 6.5.1 or the continuous-flow apparatus shown in Figure 4 and described in Section 6.5.2.

6.5.1 Jar sampler (Reference 14)—The jar sampler (Figure 3) is comprised of a heavy fluoropolymer 1-L jar with a fluoropolymer lid equipped with two 1/4 in. fluoropolymer fittings. Sample enters the jar through a short length of fluoropolymer tubing inserted into one fitting. Sample is pulled into the jar by pumping on fluoropolymer tubing attached to the other fitting. A thick

6.7 Gloves—Clean, nontalc polyethylene, latex, vinyl, or PVC; various lengths. Shoulder-length gloves are needed if samples are to be collected by direct submersion of the sample bottle into the water or when sampling for mercury.

6.7.1 Gloves, shoulder-length polyethylene—Associated Bag Co., Milwaukee, WI, 66-3-301, or equivalent.

6.7.2 Gloves, PVC—Fisher Scientific Part No. 11-394-100B, or equivalent.

6.8 Storage Bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes).

6.9 Plastic Wrap—Clean, colorless polyethylene.

6.10 Cooler—Clean, nonmetallic, with white interior for shipping samples.

6.11 Ice or Chemical Refrigerant Packs—To keep samples chilled in the cooler during shipment.

6.12 Wind Suit—Pamida, or equivalent.

NOTE: *This equipment is necessary only for collection of metals, such as mercury, that are known to have elevated atmospheric concentrations.*

6.12.1 An unlined, long-sleeved wind suit consisting of pants and jacket and constructed of nylon or other synthetic fiber is worn when sampling for mercury to prevent mercury adsorbed onto cotton or other clothing materials from contaminating samples.

6.12.2 Washing and drying—The wind suit is washed by itself or with other wind suits only in a home or commercial washing machine and dried in a clothes dryer. The clothes dryer must be thoroughly vacuumed, including the lint filter, to remove all traces of lint before drying. After drying, the wind suit is folded and stored in a clean polyethylene bag for shipment to the sample site.

6.13 Boat

6.13.1 For most situations (e.g., most metals under most conditions), the use of an existing, available boat is acceptable. A flat-bottom, Boston Whaler-type boat is preferred because sampling materials can be stored with reduced chance of tipping.

6.13.1.1 Immediately before use, the boat should be washed with water from the sampling site away from any sampling points to remove any dust or dirt accumulation.

6.13.1.2 Samples should be collected upstream of boat movement.

6.13.2 For mercury, and for situations in which the presence of contaminants cannot otherwise be controlled below detectable levels, the following equipment and precautions may be necessary:

6.15.2 Tubing—For use with peristaltic pump. SEBS resin, approximately 3/8 in. i.d. by approximately 3 ft, Cole-Parmer size 18, Cat. No. G-06464-18, or approximately 1/4 in. i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent. Tubing is cleaned by soaking in 5-10% HCl solution for 8-24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with mercury-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

6.15.3 Tubing—For connection to peristaltic pump tubing. Fluoropolymer, 3/8 or 1/4 in. o.d., in lengths as required to reach the point of sampling. If sampling will be at some depth from the end of a boom extended from a boat, sufficient tubing to extend to the end of the boom and to the depth will be required. Cleaning of the fluoropolymer can be the same as cleaning the tubing for the rotary vacuum pump (Section 6.15.1.2). If necessary, more aggressive cleaning (e.g., concentrated nitric acid) may be used.

6.15.4 Batteries to operate submersible pump—12 V, 2.6 amp, gel cell, YUASA NP2.6-12, or equivalent. A 2 amp fuse connected at the positive battery terminal is strongly recommended to prevent short circuits from overheating the battery. A 12 V, lead-acid automobile or marine battery may be more suitable for extensive pumping.

6.15.5 Tubing connectors—Appropriately sized PVC, clear polyethylene, or fluoropolymer "barbed" straight connectors cleaned as the tubing above. Used to connect multiple lengths of tubing.

6.16 Carboy—For collection and storage of dilute waste acids used to store bottles.

6.17 Apparatus—For field preservation of aliquots for trivalent chromium determinations.

6.17.1 Fluoropolymer forceps—1 L fluoropolymer jar, and 30 mL fluoropolymer vials with screw-caps (one vial per sample and blank). It is recommended that 1 mL of ultrapure nitric acid (Section 7.3) be added to each vial prior to transport to the field to simplify field handling activities (See Section 8.4.4.6).

6.17.2 Filters—0.4 µm, 47 mm polycarbonate Nuclepore (or equivalent). Filters are cleaned as follows. Fill a 1 L fluoropolymer jar approximately two-thirds full with 1 N nitric acid. Using fluoropolymer forceps, place individual filters in the fluoropolymer jar. Allow the filters to soak for 48 hours. Discard the acid, and rinse five times with reagent water. Fill the jar with reagent water, and soak the filters for 24 hours. Remove the filters when ready for use, and using fluoropolymer forceps, place them on the filter apparatus (Section 6.17.3).

6.17.3 Vacuum filtration apparatus—Millipore 47 mm size, or equivalent, vacuum pump and power source (and extension cords, if necessary) to operate the pump.

6.17.4 Eppendorf auto pipet and colorless pipet tips (100-1000 µL)

6.17.5 Wrist-action shaker—Burrel or equivalent.

chromium stock standard solution (Section 7.4.5) into a 1 L flask. Dilute to volume with 1% HCl. Store in a polyethylene bottle.

7.4.7 Ongoing precision and recovery (OPR) standard (25 µg/L)—Prepared by spiking 2.5 mL of the standard chromium spike solution (Section 7.4.6) into a 100 mL flask. Dilute to volume with 1% HCl. One OPR is required for every 10 samples.

8.0 Sample Collection, Filtration, and Handling

8.1 Site Selection

8.1.1 Selection of a representative site for surface water sampling is based on many factors including: study objectives, water use, point source discharges, non-point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, and the presence of structures (bridges, dams, etc.). When collecting samples to determine ambient levels of trace metals, the presence of potential sources of metal contamination are of extreme importance in site selection.

8.1.2 Ideally, the selected sampling site will exhibit a high degree of cross-sectional homogeneity. It may be possible to use previously collected data to identify locations for samples that are well mixed or are vertically or horizontally stratified. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing. Horizontal mixing occurs in constrictions in the channel. In the absence of turbulent areas, the selection of a site that is clear of immediate point sources, such as industrial effluents, is preferred for the collection of ambient water samples (Reference 19).

8.1.3 To minimize contamination from trace metals in the atmosphere, ambient water samples should be collected from sites that are as far as possible (e.g., at least several hundred feet) from any metal supports, bridges, wires or poles. Similarly, samples should be collected as far as possible from regularly or heavily traveled roads. If it is not possible to avoid collection near roadways, it is advisable to study traffic patterns and plan sampling events during lowest traffic flow (Reference 7).

8.1.4 The sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of trace metals first, finishing with the samples known or suspected to contain the highest concentrations. For example, if samples are collected from a flowing river or stream near an industrial or municipal discharge, the upstream sample should be collected first, the downstream sample collected second, and the sample nearest the discharge collected last. If the concentrations of pollutants is not known and cannot be estimated, it is necessary to use precleaned sampling equipment at each sampling location.

8.2 Sample Collection Procedure—Before collecting ambient water samples, consideration should be given to the type of sample to be collected, the amount of sample needed, and the devices to be used (grab, surface, or subsurface samplers). Sufficient sample volume

To minimize unnecessary confusion, it is recommended that a third team member be available to complete the necessary sample documentation (e.g., to document sampling location, time, sample number, etc). Otherwise, "dirty hands" must perform the sample documentation activity (Reference 7).

8.2.4 Extreme care must be taken during all sampling operations to minimize exposure of the sample to human, atmospheric, and other sources of contamination. Care must be taken to avoid breathing directly on the sample, and whenever possible, the sample bottle should be opened, filled, and closed while submerged.

8.2.5 Manual collection of surface samples directly into the sample bottle.

8.2.5.1 At the site, all sampling personnel must put on clean gloves (Section 6.7) before commencing sample collection activity, with "clean hands" donning shoulder-length gloves. If samples are to be analyzed for mercury, the sampling team must also put their precleaned wind suits on at this time. Note that "clean hands" should put on the shoulder-length polyethylene gloves (Section 6.7.1) and both "clean hands" and "dirty hands" should put on the PVC gloves (Section 6.7.2).

8.2.5.2 "Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.

8.2.5.3 Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.

8.2.5.4 "Clean hands" unscrews the cap and, while holding the cap upside down, discards the dilute acid solution from the bottle into a carboy for wastes (Section 6.16) or discards the reagent water directly into the water body.

8.2.5.5 "Clean hands" then submerges the sample bottle, and allows the bottle to partially fill with sample. "Clean hands" screws the cap on the bottle, shakes the bottle several times, and empties the rinsate away from the site. After two more rinsings, "clean hands" holds the bottle under water and allows bottle to fill with sample. After the bottle has filled (i.e., when no more bubbles appear), and while the bottle is still inverted so that the mouth of the bottle is underwater, "clean hands" replaces the cap of the bottle. In this way, the sample has never contacted the air.

8.2.5.6 Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.

8.2.5.7 "Dirty hands" zips the outer bag.

8.2.5.8 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.6.10 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.6.11 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedures described in Section 8.3.

8.2.7 Depth sampling using a jar sampling device (Figure 3 and Section 6.5.1)

8.2.7.1 The sampling team puts on gloves (and wind suits, if applicable) and handles bottles as with manual collection (Sections 8.2.5.1 through 8.2.5.4 and 8.2.5.6 through 8.2.5.7).

8.2.7.2 "Dirty hands" removes the jar sampling device from its storage container and opens the outer polyethylene bag.

8.2.7.3 "Clean hands" opens the inside polyethylene bag and removes the jar sampling apparatus. Ideally, the sampling device will have been preassembled in a class 100 clean room at the laboratory. If, however, it is necessary to assemble the device in the field, "clean hands" must perform this operation, described in Section 6.5.2, inside a field-portable glove bag (Section 6.6).

8.2.7.4 While "dirty hands" is holding the jar sampling apparatus, "clean hands" connects the pump to the to the 1/4 in. o.d. flush line.

8.2.7.5 "Dirty hands" lowers the weighted sampler to the desired depth.

8.2.7.6 "Dirty hands" turns on the pump allowing a large volume (>2 L) of water to pass through the system.

8.2.7.7 After stopping the pump, "dirty hands" pulls up the line, tubing, and device and places them into either a field-portable glove bag or a large, clean plastic bag as they emerge.

8.2.7.8 Both "clean hands" and "dirty hands" change gloves.

8.2.7.9 Using the technique described in Sections 8.2.5.2 through 8.2.5.4, the sampling team removes a sample bottle from storage, and "clean hands" places the bottle into the glove bag.

8.2.7.10 "Clean hands" tips the sampling jar and dispenses the sample through the short length of fluoropolymer tubing into the sample bottle.

8.2.7.11 Once the bottle is filled, "clean hands" replaces the cap of the bottle, returns the bottle to the inside polyethylene bag, and zips the bag. "Clean hands" returns the zipped bag to the outside polyethylene bag held by "dirty hands."

8.2.7.12 "Dirty hands" zips the outside bag. If the sample is to be analyzed for dissolved metals, it is filtered as described in Section 8.3.

8.3.1 Set up the filtration system inside the glove bag, using the shortest piece of pump tubing as is practicable. Place the peristaltic pump immediately outside of the glove bag and poke a small hole in the glove bag for passage of the tubing. Also, attach a short length of tubing to the outlet of the capsule filter.

8.3.2 "Clean hands" removes the water sample from the inner storage bag using the technique described in Sections 8.2.5.2 through 8.2.5.4 and places the sample inside the glove bag. "Clean hands" also places two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.

8.3.3 "Clean hands" removes the lid of the reagent water bottle and places the end of the pump tubing in the bottle.

8.3.4 "Dirty hands" starts the pump and passes approximately 200 mL of reagent water through the tubing and filter into the waste bottle. "Clean hands" then moves the outlet tubing to a clean bottle and collects the remaining reagent water as a blank. "Dirty hands" stops the pump.

8.3.5 "Clean hands" removes the lid of the sample bottle and places the intake end of the tubing in the bottle.

8.3.6 "Dirty hands" starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump. "Clean hands" uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.

8.3.7 "Dirty hands" starts the pump and the remaining sample is processed through the filter and collected in the sample bottle. If preservation is required, the sample is acidified at this point (Section 8.4).

8.3.8 "Clean hands" replaces the lid on the bottle, returns the bottle to the inside bag, and zips the bag. "Clean hands" then places the zipped bag into the outer bag held by "dirty hands."

8.3.9 "Dirty hands" zips the outer bag, and places the double-bagged sample bottle into a clean, ice-filled cooler for immediate shipment to the laboratory.

NOTE: *It is not advisable to reclean and reuse filters. The difficulty and risk associated with failing to properly clean these devices far outweighs the cost of purchasing a new filter.*

8.4 Preservation

8.4.1 Field preservation is not necessary for dissolved metals, except for trivalent and hexavalent chromium, provided that the sample is preserved in the laboratory and allowed to stand for at least two days to allow the metals adsorbed to the container walls to redissolve. Field preservation is advised for hexavalent chromium in order to provide sample stability for up to 30 days. Mercury samples should be shipped by overnight courier and preserved when received at the laboratory.

8.4.5.1 Decant 125 mL of sample into a clean polyethylene bottle.

8.4.5.2 Prepare an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section 7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL NaOH to each 125 mL sample and blank aliquot.

8.4.5.3 Cap the vial(s) and double-bag for shipment to the laboratory.

9.0 Quality Assurance/Quality Control

9.1 The sampling team shall employ a strict quality assurance/ quality control (QA/QC) program. The minimum requirements of this program include the collection of equipment blanks, field blanks, and field replicates. It is also desirable to include blind QC samples as part of the program. If samples will be processed for trivalent chromium determinations, the sampling team shall also prepare method blank, OPR, and MS/MSD samples as described in Section 9.6.

9.2 The sampling team is permitted to modify the sampling techniques described in this method to improve performance or reduce sampling costs, provided that reliable analyses of samples are obtained and that samples and blanks are not contaminated. Each time a modification is made to the procedures, the sampling team is required to demonstrate that the modification does not result in contamination of field and equipment blanks. The requirements for modification are given in Sections 9.3 and 9.4. Because the acceptability of a modification is based on the results obtained with the modification, the sampling team must work with an analytical laboratory capable of making trace metals determinations to demonstrate equivalence.

9.3 Equipment Blanks

9.3.1 Before using any sampling equipment at a given site, the laboratory or equipment cleaning contractor is required to generate equipment blanks to demonstrate that the equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampling equipment blanks.

9.3.2 Equipment blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and the jar sampling device, then an equipment blank must be run on both pieces of equipment.

9.3.3 Equipment blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the equipment using the same procedures that are used in the field (Section 8.0). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility. In addition, training programs must require must require sampling personnel to collect a clean equipment blank before performing on-site field activities.

9.3.4 Detailed procedures for collecting equipment blanks are given in the analytical methods referenced in Table 1.

9.3.5 The equipment blank must be analyzed using the procedures detailed in the

9.6 Additional QC for Collection of Trivalent Chromium Aliquots

9.6.1 Method blank—The sampling team must prepare one method blank for every ten or fewer field samples. Each method blank is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on a 100 mL aliquot of reagent water (Section 7.1). Do not use the procedures in Section 8.3 to process the method blank through the 0.45 µm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.

9.6.2 Ongoing precision and recovery (OPR)—The sampling team must prepare one OPR for every ten or fewer field samples. The OPR is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on the OPR standard (Section 7.4.7). Do not use the procedures in Section 8.3 to process the OPR through the 0.45 µm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.

9.6.3 MS/MSD—The sampling team must prepare one MS and one MSD for every ten or fewer field samples.

9.6.3.1 If, through historical data, the background concentration of the sample can be estimated, the MS and MSD samples should be spiked at a level of one to five times the background concentration.

9.6.3.2 For samples in which the background concentration is unknown, the MS and MSD samples should be spiked at a concentration of 25 µg/L.

9.6.3.3 Prepare the matrix spike sample by spiking a 100-mL aliquot of sample with 2.5 mL of the standard chromium spike solution (Section 7.4.6), and processing the MS through the steps in Sections 8.4.4.1 through 8.4.4.6.

9.6.3.4 Prepare the matrix spike duplicate sample by spiking a second 100-mL aliquot of the same sample with 2.5 mL of the standard chromium spike solution, and processing the MSD through the steps in Sections 8.4.4.1 through 8.4.4.6.

9.6.3.5 If field samples are collected for dissolved metals determinations, it is necessary to process an MS and an MSD through the 0.45 µm filter as described in Section 8.3.

10.0 Recleaning the Apparatus Between Samples

10.1 Sampling activity should be planned so that samples known or suspected to contain the lowest concentrations of trace metals are collected first with the samples known or suspected to contain the highest concentrations of trace metals collected last. In this manner, cleaning of the sampling equipment between samples in unnecessary. If it is not possible to plan sampling activity in this manner, dedicated sampling equipment should be provided for each sampling event.

10.2 If samples are collected from adjacent sites (e.g., immediately upstream or downstream), rinsing of the sampling Apparatus with water that is to be sampled should be sufficient.

14.0 References

1. Adeloju, S.B. and Bond, A.M. "Influence of Laboratory Environment on the Precision and Accuracy of Trace Element Analysis," *Anal. Chem.* **1985**, *57*, 1728.

2. Berman, S.S. and Yeats, P.A. "Sampling of Seawater for Trace Metals," *CRC Reviews in Analytical Chemistry* **1985**, *16*.

3. Bloom, N.S. "Ultra-Clean Sampling, Storage, and Analytical Strategies for the Accurate Determination of Trace Metals in Natural Waters." Presented at the 16th Annual EPA Conference on the Analysis of Pollutants in the Environment, Norfolk, VA, May 5, 1993.

4. Bruland, K.W. "Trace Elements in Seawater," *Chemical Oceanography* **1983**, *8*, 157.

5. Nriagu, J.O., Larson, G., Wong, H.K.T., and Azcue, J.M. "A Protocol for Minimizing Contamination in the Analysis of Trace Metals in Great Lakes Waters," *J. Great Lakes Research* **1993**, *19*, 175.

6. Patterson, C.C. and Settle, D.M. "Accuracy in Trace Analysis," in *National Bureau of Standards Special Publication 422*; LaFleur, P.D., Ed., U.S. Government Printing Office, Washington, DC, 1976.

7. "A Protocol for the Collection and Processing of Surface-Water Samples for Subsequent Determination of Trace Elements, Nutrients, and Major Ions in Filtered Water"; Office of Water Quality Technical Memorandum 94.09, Office of Water Quality, Water Resources Division, U.S. Geological Survey, Reston, VA, Jan. 28, 1994.

8. Standard Operating Procedure No. 4-54, Revision 01, *SOP for Concentration and Analysis of Chromium Species in Whole Seawater;* Prepared by Battelle Ocean Sciences, Duxbury, MA for the U.S. Environmental Protection Agency Office of Marine Environmental Protection, Ocean Incineration Research Program, 1987.

9. Cranston, R.E. and Murray, J.W. "The Determination of Chromium Species in Natural Waters," *Anal. Chem. Acta* **1978**, *99*, 275.

10. Prothro, M.G. "Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria"; EPA Memorandum to Regional Water Management and Environmental Services Division Directors, Oct. 1, 1993.

11. "Format for Method Documentation"; Distributed by the EPA Environmental Monitoring Management Council, Washington, DC, Nov. 18, 1993.

12. Windom, H.L., Byrd, J.T., Smith, R.G., Jr., and Huan, F. "Inadequacy of NASQAN Data for Assessing Metal Trends in the Nation's Rivers," *Environ. Sci. Technol.* **1991**, *25*, 1137.

13. Zief, M. and Mitchell, J.W. "Contamination Control in Trace Metals Analysis," *Chemical Analysis* **1976**, *47*, Chapter 6.

14. Phillips, H., Shafer, M., Dean, P., Walker, M., and Armstrong, D. "Recommendations for Trace Metals Analysis of Natural Waters"; Wisconsin Department of Natural Resources: Madison, WI, May 1992.

inlet sampler or by splitting a larger aliquot and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

15.6 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)—Aliquots of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.

15.7 May—This action, activity, or procedural step is optional.

15.8 May Not—This action, activity, or procedural step is prohibited.

15.9 Minimum Level (ML)—The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point (Reference 21).

15.10 Must—This action, activity, or procedural step is required.

15.11 Reagent Water—Water demonstrated to be free from the metal(s) of interest and potentially interfering substances at the MDL for that metal in the referenced method or additional method.

15.12 Should—This action, activity, or procedural step is suggested but not required.

15.13 Trace-Metal Grade—Reagents that have been demonstrated to be free from the metal(s) of interest at the method detection limit (MDL) of the analytical method to be used for determination of this metal(s).

The term "trace-metal grade" has been used in place of "reagent grade" or "reagent" because acids and other materials labeled "reagent grade" have been shown to contain concentrations of metals that will interfere in the determination of trace metals at levels listed in Table 1.

TABLE 2. ANALYTES, PRESERVATION REQUIREMENTS, AND CONTAINERS

Metal	Preservation Requirements	Acceptable Containers
Antimony Arsenic Cadmium Copper Lead Nickel Selenium Silver Thallium Zinc	Add 5 mL of 10% $HN0_3$ to 1-L sample; preserve on-site or immediately upon laboratory receipt.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (III)	Add 1 mL chromium (III) extraction solution to 100 mL aliquot, vacuum filter through 0.4 µm membrane, add 1 mL 10% $HN0_3$; preserve on-site immediately after collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (IV)	Add 50% NaOH; preserve immediately after sample collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Mercury	Total: Add 0.5% high-purity HCl or 0.5% BrCl to pH < 2; Total & Methyl: Add 0.5% high-purity HCL; preserve on-site or immediately upon laboratory receipt	Fluoropolymer or borosilicate glass bottles with fluoropolymer or fluoropolymer-lined caps

Figure 2 - Grab Sampling Device

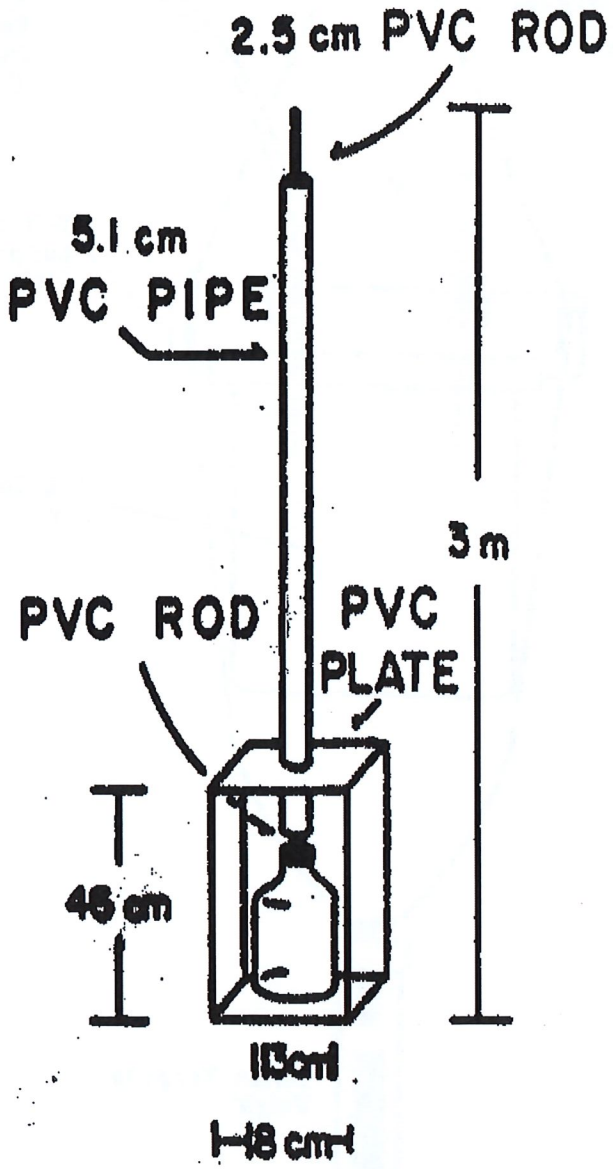
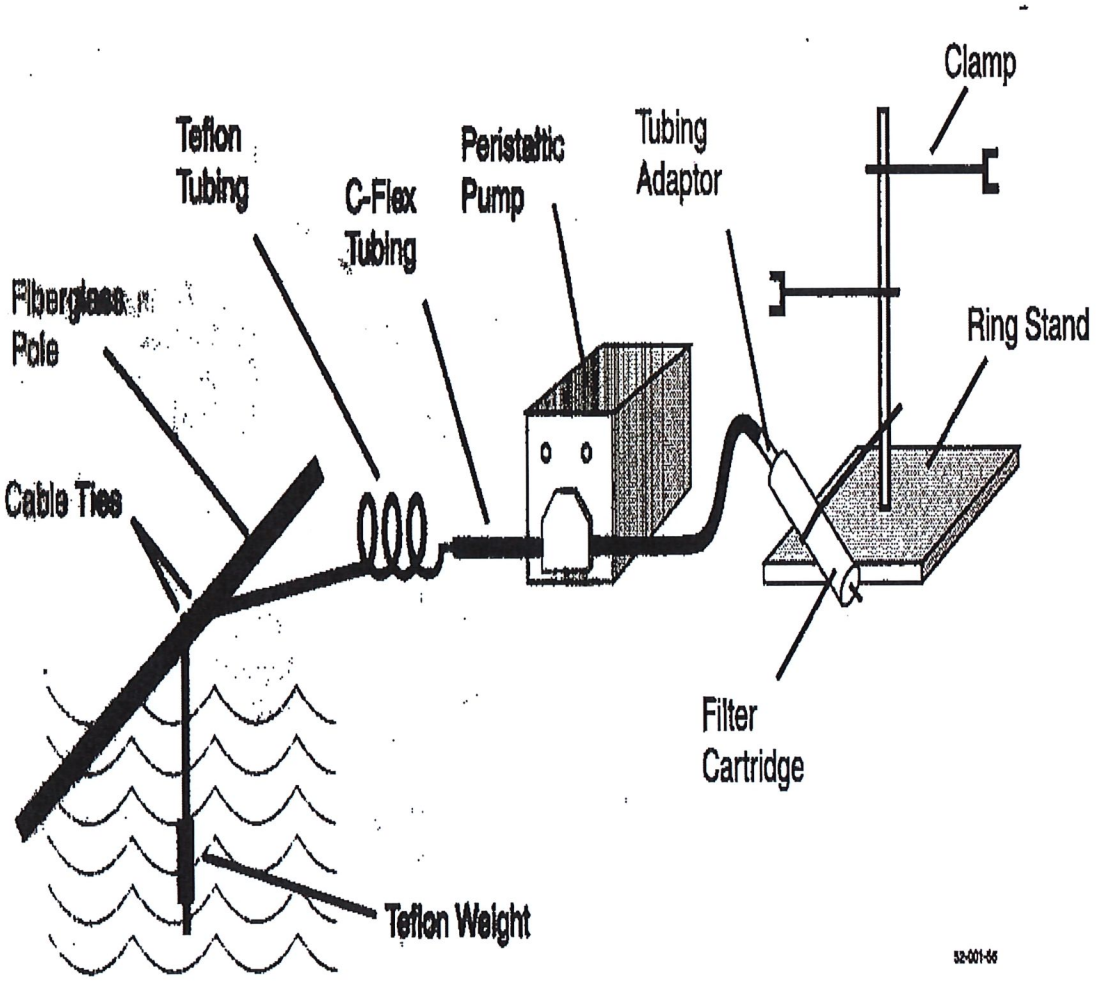


Figure 4 - Sample Pumping System



APPENDIX F

EnviroSystems Laboratory Chain-of-Custody

ESI

EnviroSystems, Inc.
1 Lafayette Road
Hampton, NH 03842

Voice: 603-926-3345
FAX: 603-926-3521

ESI Job No:

CHAIN OF CUSTODY DOCUMENTATION

Client:	Contact:	Project Name:	
Report to:	Address:	Project Number:	Task:
Invoice to:	Address:	Project Manager:	
Voice:	Fax:	email:	P.O. No: Quote No:

Protocol:

Lab Number (assigned by lab)	Your Field ID: (must agree with container)	Date Sampled	Time Sampled	Sampled By	Grab or com-posite (G/C)	Container No	Container Size (mL)	Container Type (P/G/T)	Field Preser-vation	Matrix S=Solid W=Water	FIlter N=Not needed F=Done in field L=Lab to do	Analyses Requested\ Special Instructions:

Relinquished By:	Date:	Time:	Received By: Date: Time:
Relinquished By:	Date:	Time:	Received at Lab By: Date: Time:

Comments:

COC Number: A1000041

Sample Delivery Group No:

Page of

APPENDIX G

NH Volunteer River Assessment Program

Water Quality Monitoring Sampling Protocols for Volunteer Monitors

NH Volunteer River Assessment Program

Water Quality Monitoring Sampling Protocols For Volunteer Monitors

LaMotte 2020e Turbidity Meter

Oakton pH 11 Meter

YSI 85 Water Temperature/Dissolved Oxygen/Conductivity Meter

New Hampshire Department of Environmental Services
29 Hazen Drive / PO Box 95
Concord, NH 03302-0095
http://des.nh.gov/organization/divisions/water/wmb/vrap/index.htm

May 2012

Introduction: What is VRAP?

The New Hampshire Volunteer River Assessment Program (VRAP) was established in 1998 to promote awareness and education of the importance of maintaining water quality in New Hampshire's rivers and streams. VRAP aims to educate people about river and stream water quality and ecology and to improve water quality monitoring coverage for the protection of water resources.

Today, VRAP loans water quality monitoring equipment, provides technical support, and facilitates educational programs to volunteer groups on numerous rivers and watersheds throughout the state. These groups conduct water quality monitoring on an ongoing basis and increase the amount of river water quality information available to local, state and federal governments, which allows for better watershed planning.

This manual is meant to be used as a guide for VRAP monitors. Take this manual with you in the field as a reminder of the proper sampling procedures. Each meter has a very important calibration procedure which must be followed to ensure the sampling results are as accurate as possible. If you encounter problems during calibration, refer to the manufacturer's operation manuals or contact the VRAP staff.

This manual is also designed to compliment the annual VRAP volunteer training workshop and is not a replacement for attending a training workshop. VRAP staff are also available to visit with each group in the field. Please contact us to schedule a visit.

Informational Resources

- **Water Quality Monitoring Field Sampling Protocols:**
  http://des.nh.gov/organization/divisions/water/wmb/vrap/categories/publications.htm
- **A Quick-Reference Guide to Water Quality Monitoring:**
  http://des.nh.gov/organization/divisions/water/wmb/vrap/documents/quick-ref-guide-wq-monitor.pdf
- **VRAP Field Data Sheet:**
  http://des.nh.gov/organization/divisions/water/wmb/vrap/documents/field_data_sheet.pdf
- **Volunteer Monitor Field Sampling Procedures Self Assessment:**
  http://des.nh.gov/organization/divisions/water/wmb/vrap/documents/self-assessment-form.pdf
- **Laboratory Services Login & Custody Sheet:**
  http://des.nh.gov/organization/divisions/water/wmb/vrap/documents/lab-login.doc
- **A Quick-Reference Guide to Water Quality Standards**
  http://des.nh.gov/organization/divisions/water/wmb/vrap/documents/wq_standards.pdf
- **Interpreting VRAP Water Quality Parameters:**
  http://des.nh.gov/organization/commissioner/pip/publications/wd/documents/vrap_parameters.pdf
- **Troubleshooting Guide to VRAP Water Quality Meters:**
  http://des.nh.gov/organization/divisions/water/wmb/vrap/documents/troubleshooting_meters.pdf

Quality Assurance & Quality Control

In order for VRAP data to be used in the assessment of New Hampshire's surface waters, the data must meet quality control guidelines as outlined in the VRAP Quality Assurance Project Plan (QAPP). The QAPP is reviewed annually and is officially updated and approved every five years. The VRAP Quality Assurance/Quality Control (QA/QC) measures include a six-step approach to ensuring the accuracy of the equipment and consistency in sampling efforts.

1. Calibration

- Calibrate the pH and dissolved oxygen meters prior to each measurement of the day.
- Check the conductivity meter against a known standard prior to the first measurement of the day. Check and calibrate the turbidity meter against a known standard prior to the first measurement of the day.

2. Replicate Analysis

- Measure and record a second measurement by each meter from the original sample at one of the stations during the sampling day. Replicates should be measured within 15 minutes of the original measurements. If more than one team is out sampling each team should complete a replicate analysis.

3-5. QA/QC Meter Checks

- **6.0 pH Standard:** Measure and record a reading of the 6.0 pH buffer at one of the stations during the sampling day. Do not calibrate the meter prior to this measurement as it is intended to detect drift in the meter
- **Zero Oxygen Solution:** Measure and record a reading of a zero oxygen solution at one of the stations during the sampling day. The dissolved oxygen concentration value should be below 1.0 mg/L.
- **DI (De-Ionized) Turbidity Blank**: Measure and record a reading of the DI turbidity blank (0 NTU) at one of the stations during the sampling day.

6. End of the Day Conductivity & Turbidity Meter Checks

- Re-check and record a reading of the conductivity and turbidity meters against a known standard at the conclusion of each sampling day.

Please Note

- If the same sampling schedule is used throughout the monitoring season, the Replicate Analysis and QA/QC Meter Checks should be conducted at different stations.

Order of Field Tests

- Pour and/or collect samples for laboratory analysis
- Turbidity
- pH
- Water Temperature, Dissolved Oxygen
- Specific Conductance

Collecting Samples for Field Analysis

Please label all bottles *prior to filling them* with the following information: NHDES Station ID, date and time of collection, test(s) required, and collector's initials.

Begin with the most downstream sampling station so that sampling activities do not affect water quality at downstream stations.

Method 1: Bridge Sampling

1. Lower the bucket into the river from the **upstream** side of the bridge (water flowing toward you).
2. Fill ¼ of the bucket with water.
3. Pull the bucket up, swish the water around in it to rinse, and discard the rinse water off the downstream/opposite side of the bridge. Repeat this process two more times.
3. Return the bucket into the river from the upstream side of the bridge and slowly fill ½ - ¾ of the bucket with water (you may wish to weight one side of the bucket).
4. Slowly pull up the bucket with sample water. Do not to bump the bucket against the bridge or otherwise agitate the sample water in the bucket as this may introduce additional oxygen and sediment and may yield inaccurate readings.
5. Carefully carry the sample to a safe location for analyses. Do not place the sample bucket in direct sunlight or on hot pavement as this may alter water temperature and dissolved oxygen measurements and may yield inaccurate readings.

Method 2: Offshore Sampling

1. Carefully wade out into the river as close as possible to the center (to collect the most representative sample). Do not enter water above your waist and be sure someone on shore knows where you are.
2. Facing **upstream** (water flowing toward you), rinse the bucket with water. Do not collect the water that is running over your legs/boots. Discard the rinse water behind you, downstream. Repeat this process two more times.
3. With the bucket held in front of you, dip the lip of the bucket into the flowing water slowly fill ½ - ¾ of the bucket with water.
4. Carefully carry the sample to a safe location for analyses. Do not place the sample bucket in direct sunlight or on hot pavement as this may alter water temperature and dissolved oxygen measurements and may yield inaccurate readings.

Collecting Samples for Laboratory Analysis

Completing the NHDES Laboratory Services Login & Custody Sheet

VRAP staff is available to assist you with the login procedure for laboratory samples. Please contact the VRAP Coordinator prior to relinquishing samples at NHDES. The following is a guideline for how to complete the NHDS Laboratory Services Login & Custody Sheet which is required to be submitted along with your samples.

- **Client ID:** Please leave blank.
- **Lab Account (Billing):** Please write in either your group's laboratory account number or the VRAP lab account number which is 05-0022518
- **One Stop Project:** Please write in "VRAP".
- **NHDES Site Number:** Please leave blank.
- **Description:** Please write in your river or watershed name.
- **Town:** Please leave blank.
- **Collected By:** Please write in the name and phone number of the person who should be contacted if there are any questions about the samples.
- **Contact & Phone Number:** Please write in the VRAP Contact name and phone number.
- **Sample Location/Station ID:** Please use NHDES VRAP Station IDs. If the ID is not exactly the same as the one in our database it holds up the reporting of the results of the entire sampling batch which was relinquished.
- Common mistakes include not including a zero where it is needed (1-BKB instead of 01-BKB), adding text to the end of the station ID (00M-BKB Front Street instead of just 00M-BKB), and forgetting to include the dash between the number and Station ID or REP for replicates (01BKB instead of 01-BKB or 01-BKBREP instead of 01-BKB-REP).
- **Date/Time Sampled:** Please write the date and time of each sample collected.
- **# of Containers:** Please list the number of sample bottles per station.
- **Matrix:** Please write "AQ" for aqueous.
- In the columns to the right of the "Matrix" column, please write in the parameter to be analyzed. (For example TP, TKN, *E.coli*, chloride, nitrate, etc.)
- **Sampler Comments:** Please leave blank.
- **Lab Login #.** Please leave blank.
- **Relinquished By:** Please sign your name on the top line and leave the bottom line blank.
- **Date & Time:** Please write the date and time you relinquished the samples on the top line and leave the bottom line blank. If you measured field parameters, the time(s) on the Login & Custody sheet should match the time(s) on the VRAP Field Data Sheet.
- **Received By:** Please leave blank. This will be completed by the NHDES Laboratory Services personnel.

Please fill in the number of pages (Example: Page 1 of 1) at the bottom of the sheet.

5. Fill the sample vial with river water by carefully and slowly pouring the water down the side of the sample vial to avoid introducing any bubbles.

6. Wipe any water, dust and/or fingerprints off the sample vial with a Kimwipe. **Note: Any residue on the vials will interfere with an accurate turbidity reading. Anything other than Kimwipes may scratch the vials, causing inaccurate readings.**

7. Open the lid of the turbidimeter and align the single, squared-off notch (or the vertical white line located on the vial) on the cleaned sample vial with the vertical, white indexing line that is printed on the tube.

8. If the meter is turned off, turn it **ON** and select **MEASURE** mode by pressing ***OK**.

9. If the meter is already **ON**, ensure you scroll down so the meter reads "Scan Sample" (otherwise the meter will read "Scan Blank").

10. **SCAN SAMPLE** by pressing ***OK.**

11. **Record** the displayed turbidity value on the VRAP Field Data Sheet.

12. If the turbidity value is great than 10 NTU you should recalibrate the meter with the 10 NTU standard and take another reading. This will give a more accurate measurement of how high the turbidity level is. If you do recalibrate with the 10 NTU standard, be sure to indicate this under the "Comments" section on the back the VRAP Field Data Sheet. **Recalibrate with the 1.0 NTU at the next station to prevent the readings from being artificially elevated.**

13. Turn the meter **OFF**. Remove the sample vial, empty it and rinse with DI water. Fill the sample vial with DI water.

QA/QC Meter Check

1. At one of the stations during the sampling day measure and record a reading of the DI Turbidity Blank (0.0 NTU) standard. If the same sampling schedule is used throughout the monitoring season, the blank check should be conducted at different stations.

2. **Record** the value, station, and time on the VRAP Field Data Sheet.

End of the Day Meter Check

1. At the end of the day, read the 1.0 standard.

2. **Record** the value under the **"End of Day Meter Check"** on the VRAP Field Data Sheet.

3. Turn the meter off.

4. **Rinse** the sample vial with DI water and fill the vial with DI water for storage.

16. Press the **HOLD/ENTER** button. The display shows the electrode offset mV value. If you have not calibrated at any buffer, the primary display shows "---".

17. Press the **HOLD/ENTER** key again to proceed to electrode slope display. The display shows electrode slope in percentage.

18. **Record** the slope on the VRAP Field Data Sheet

19. To return to **MEAS** mode press the CAL/MEAS button twice.

20. The meter will proceed to the measure mode; **MEAS** is displayed above the main display field. The meter is now ready for use.

Measuring pH

Note: The pH meter must be calibrated prior to each measurement (at each station) including a replicate.

1. Remove the probe, **rinse** with DI water and blot the plastic areas dry with a Kimwipe. **CAUTION:** Be sure to never touch the glass bulb/measurement end; even with a Kimwipe.
2. Immerse the pH probe into the small plastic sample container. The meter should be in the **MEAS** mode. Submerge the bottom two inches of the electrode and agitate by slowly moving the electrode back and forth in the sample for the pH reading to stabilize (this should take approximately two minutes).
3. Wait for the **READY** indicator to be displayed and record the value on the VRAP Field Data Sheet. The READY indicator may blink on and off. It is important to wait until drifting of the pH value has stopped before recording measurement.
4. **Rinse** the probe with DI water and return it to the electrode solution storage container. Ensure the pH electrode storage container is filled about halfway with pH storage solution. Be careful not to push the electrode against the bottom of the container as this could damage the electrode. **Never store pH probe in DI water!**
5. Turn the meter **OFF** and return the meter and the probe to its kit.

QA/QC Meter Check

1. At one of the stations during the sampling day measure and record a reading of the 6.0 pH buffer. If the same sampling schedule is used throughout the monitoring season, the blank check should be conducted at different stations.
2. **Record** the value, station, and time on the VRAP Field Data Sheet.

End of the Day

1. Turn the meter off. **Rinse** the probe with DI water and blot dry with a Kimwipe.
2. Return the probe to the storage solution container. Store probe upright.

4. **Rinse** the probe with DI water and blot dry with a Kimwipe. Gently shake the probe to remove water from the oval upper conductivity opening.

5. Submerge the entire probe in **conductivity standard solution**, and allow to stabilize. Ensure there is enough solution to cover the top opening of the probe.

6. Record the **"Initial Conductivity Meter Check Value"** on the top left of the VRAP Field Data Sheet. A 20% error regardless of the standard used (1,600 – 2,400µS for 2,000µS standard, 160-240µS for 200µS standard or 80µS - 120µS for 100µS standard) is acceptable. If the reading is outside of this range, please check again with new standard if available. If new standard is unavailable please sample anyway and contact VRAP staff as soon as possible.

7. **Rinse** the probe with DI water and return it to the storage chamber.

Wait 15 Minutes with Probe in Chamber Prior to Calibration

1. Ensure the meter has been turned ON with the probe in its chamber for at least 15 minutes before calibrating.

Before Sampling: Calibrate the Meter for Dissolved Oxygen

Note: The Dissolved Oxygen/Temperature meter must be calibrated prior to <u>each</u> DO measurement (each station) including a replicate.

1. **Record** the time of the first dissolved oxygen calibration on the upper right front page of the VRAP Field Data Sheet.

2. Press the **MODE** button until dissolved oxygen is displayed in % saturation. The **MODE** button on the YSI 85 can be used to toggle back and forth between % saturation and mg/L however, the YSI 85 will also cycle through the specific conductance modes.

3. Press and release both the **DOWN** and **UP** arrow buttons (DOWN slightly prior to UP) to enter the DO/Temperature meter calibration menu. You will see **CAL** in the lower left hand corner when you have successfully entered calibration mode.

4. The screen will prompt you to enter the local altitude in hundreds of feet. Use the **UP** and **DOWN** arrows to adjust the value appropriately (For example, entering a 12 indicates 1200 feet above sea level) and press **ENTER**.

5. **Record** the dissolved oxygen calibration value **(displayed on the bottom right-corner of the LCD screen)** on the VRAP Field Data Sheet. The calibration value will vary with altitude and thus may be different at each station if the altitude varies.

6. Press **ENTER** again. The display should read **SAVE** and then return to normal measurement mode.

7. Wait approximately one minute for dissolved oxygen % saturation to stabilize. Once it has stabilized, record the dissolved oxygen % saturation (chamber reading) on the VRAP Field Data Sheet. If drift occurs (goes up or down by more than 5%) ensure you have waited long enough for the reading to stabilize. If drift still occurs, recalibrate.

8. **Leave the meter on until you are finished with all measurements for the day. Calibration must be repeated before <u>each</u> individual measurement. If the meter shuts off, you must wait 15 minutes with the probe in its chamber before calibrating.**

End of the Day Meter Check

1. Ensure the meter is in the temperature compensated specific conductance mode by pressing **MODE** until the **°C** is flashing to indicate this mode.

2. **Rinse** the probe with DI water and blot dry with a Kimwipe. Gently shake the probe to remove water from the oval upper conductivity opening.

3. Submerge the entire probe in the **conductivity standard solution**, and allow to stabilize. Ensure there is enough solution to cover the top opening of the probe.

4. **Record** the **"End of the Day Meter Check"** value on the VRAP Field Data Sheet. A 20% error regardless of the standard used (1,600 – 2,400µS for 2,000µS standard, 160-240µS for 200µS standard or 80µS - 120µS for 100µS standard) is acceptable. If the reading is outside of this range, please check again with new standard if available. If new standard is unavailable please contact VRAP staff as soon as possible.

End of the Day

1. **Rinse** the probe with DI water.

2. Return the probe to the chamber with a wet sponge. Drain any water from the chamber.

3. Turn the meter off.